(54) Title: VANADIUM OXIDE PARTICLES AND BATTERIES WITH ELECTROACTIVE NANOPARTICLES

(57) Abstract

Vanadium oxide nanoparticles with different vanadium oxidation states and different crystal structures. The particles have a narrow distribution of particle diameters and unique properties that result from their small size and correspondingly large surface area. The particles are produced by laser pyrolysis, and can be further treated to change their properties, without destroying their nanoscale size. The stoichiometry and crystal structure can be varied by initial heating under mild conditions. The materials may be used as cathode active materials in high energy density batteries.

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VANADIUM OXIDE PARTICLES AND BATTERIES WITH ELECTROACTIVE NANOPARTICLES

FIELD OF THE INVENTION

The invention relates to nanoscale vanadium
5   oxide particles. The invention further relates to the
production of nanoscale vanadium oxide particles using
laser pyrolysis and the conversion of the stoichiometry
and/or crystal structure of vanadium oxide particles by
applying heat. The invention further relates to
10 batteries, especially lithium batteries and lithium ion
batteries, incorporating nanoparticles, such as vanadium
oxide nanoparticles, as an electroactive material.

BACKGROUND OF THE INVENTION

Vanadium can exist in various oxidation
15 states. Correspondingly, vanadium oxides are known to
exist with various stoichiometries. In addition,
vanadium oxides with a particular stoichiometry can have
various crystalline lattices, or they can be amorphous.
Thus, vanadium oxides exhibit an extraordinarily rich
20 phase diagram.

Vanadium oxides with various stoichiometries
have been noted as promising materials for use in
lithium based batteries. Appropriate vanadium oxides
can intercalate lithium ions into their crystal
25 structure. In addition, vanadium oxides are useful in
a variety of other applications, for example, as
catalysts for chemical reactions. Because of the
interest in vanadium oxides, several approaches have
been developed for producing vanadium oxides.

30   The microminiaturization of electronic
components has created widespread growth in the use of
portable electronic devices such as cellular phones,
pagers, video cameras, facsimile machines, portable

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stereophonic equipment, personal organizers and personal computers. The growing use of portable electronic equipment has created ever increasing demand for improved power sources for these devices. Relevant
5   batteries include primary batteries, i.e., batteries designed for use through a single charging cycle, and secondary batteries, i.e., batteries designed to be rechargeable. Some batteries designed essentially as primary batteries may be rechargeable to some extent.
10   Batteries based on lithium have been the subject of considerable development effort and are being sold commercially. Lithium based batteries generally use electrolytes containing lithium ions. The anodes for these batteries can include lithium metal (lithium
15   batteries), or compositions that intercalate lithium (lithium ion batteries). Preferred electroactive materials for incorporation into the cathodes are compositions that intercalate lithium. The compositions that intercalate lithium, for use in the cathodes,
20   generally are chalcogenides such as metal oxides that can incorporate the lithium ions into their lattice. Vanadium oxides are examples of promising compounds for the production of cathodes because of their high theoretical energy densities.
25   SUMMARY OF THE INVENTION
          In one aspect, the invention features a collection of particles including vanadium oxide, the measurements along the principle axes of the particles are each about 1000 nm or less for at least about 95
30   percent of the particles. The particles have an average diameter of generally about 1000 nm or less, preferably about 150 nm or less, more preferably from about 5 nm to about 100 nm, and even more preferably from about 5 nm to about 50 nm.

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The vanadium oxide nanoparticles can have a stoichiometry, for example, of VO_2, V_2O_5 or V_6O_{13} and can be amorphous or crystalline. Preferably, about 95 percent of the vanadium oxide nanoparticles have a diameter greater than about 50 percent of the average diameter and less than about 150 percent of the average diameter.

In another aspect, the invention features a method of producing vanadium oxide nanoparticles including the step of pyrolyzing a molecular stream including a vanadium precursor, an oxidizing agent and a radiation absorbing gas in a reaction chamber, where the pyrolysis is driven with heat absorbed from a laser beam. The vanadium oxide nanoparticles preferably have an average diameter from about 5 nm to about 150 nm. The laser beam preferably is produced by CO_2 laser. The radiation absorbing gas can include C_2H_4. The vanadium precursor can include $VOCl_3$, and the oxidizing agent can include O_2.

In another aspect, the invention features an apparatus including:

(a)   a reaction chamber isolated from the ambient atmosphere;

(b)   a reactant gas inlet defining a path of a molecular stream, where the reactant gas inlet is connected to a source of vanadium precursor, an oxidizing agent and a laser absorbing gas;

(c)   a laser beam path intersecting the path of the molecular stream; and

(d)   a product outlet.

The reactant gas inlet preferably is elongated in one dimension.   The apparatus can further include a CO_2

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laser aligned to produce a laser beam along the laser
beam path.

In another aspect, the invention features a
process for converting nanoparticles of vanadium oxide
5   to other forms of vanadium oxide comprising the step of
heating the nanoparticles of vanadium oxide in an
oxidizing or inert atmosphere at a temperature at least
about 300°C below the melting point of both the
nanoparticles of vanadium oxide particles and the other
10   forms of vanadium oxide. The temperature preferably is
between about 60°C and about 800 °C and more preferably
between about 60°C and about 500°C.

The heating can be performed in an oxidizing
atmosphere, which can include O_2, O_3, CO, CO_2 or
15   combinations thereof. The oxidizing atmosphere can
include between about 1 percent oxidizing gas and about
99 percent oxidizing gas by partial pressure. The
oxidizing atmosphere can include flowing gas. The
nanoparticles of vanadium oxide can include $VO_{1.27}$, VO_2,
20   V_2O_3, V_3O_5, amorphous V_2O_5, or 2-D crystalline V_2O_5. The
other forms of vanadium oxide can include 2-D
crystalline V_2O_5 or crystalline V_2O_5. The nanoparticles
of vanadium oxide preferably have an average diameter
from about 5 nm to about 500 nm or more preferably from
25   about 5 nm to about 150 nm.

In another aspect, the invention features
vanadium oxide nanoparticles formed by heating in an
oxidizing or inert atmosphere, vanadium oxide
nanoparticles of a different form. The vanadium oxide
30   nanoparticles of a different form preferably have an
average diameter from about 5 nm to about 150 nm. In
some embodiments, the vanadium oxide nanoparticles
formed by heating have a higher oxygen to vanadium ratio
than the vanadium oxide nanoparticles of a different

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form. The vanadium oxide particles formed by heating can include V_2O_5.

In another aspect, the invention features a process for forming vanadium oxide particles including the step of heating particles of vanadium oxide with a lower oxygen to vanadium ratio than the vanadium oxide particles to be formed, in an oxidizing atmosphere at a temperature at least about 300°C below the melting point of both the vanadium oxide particles to be heated and the vanadium oxide particles to be formed. The temperature preferably is between about 60°C and about 800°C, and more preferably between about 80°C and about 500°C.

The oxidizing atmosphere can comprise O_2, O_3, CO, CO_2 or combinations thereof. The oxidizing atmosphere can include from about 1 percent oxidizing gas and 99 percent oxidizing gas by partial pressure. The initial vanadium oxide particles preferably have an average diameter from about 5 nm to about 1000 nm, and more preferably from about 5 nm to about 150 nm. The product vanadium oxide particles can comprise orthorhombic V_2O_5 crystals or 2-D V_2O_5 crystals.

In another aspect, the invention features a process for forming crystalline V_2O_5 including the step of heating amorphous V_2O_5 at a temperature at least about 300°C below the melting point of both the amorphous V_2O_5 and the crystalline V_2O_5. The temperature preferably is between about 60°C and about 800°C. The amorphous V_2O_5 particles preferably have an average diameter from about 5 nm to about 1000 nm.

In another aspect, this invention features a cathode composition including vanadium oxide particles having an average diameter less than about 1000 nm and a binder. The vanadium oxide particles preferably have

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an average diameter from about 5 nm to about 150 nm and more preferably from about 5 nm to about 50 nm. The binder can be polyvinylidene fluoride, polyethylene oxide, polyethylene, polypropylene,

5   polytetrafluoroethylene, polyacrylates, mixtures thereof or copolymers thereof. The cathode composition can further include supplementary electrically conductive particles. The supplementary electrically conductive particles can include carbon. The cathode composition

10   preferably includes from about 60 percent by weight to about 98 percent by weight vanadium oxide particles.

In another aspect, the invention features a battery including an anode, a cathode comprising vanadium oxide particles having an average diameter less

15   than about 1000 nm and a binder, and a separator element disposed between the anode and cathode. The anode can include lithium metal or a composition that intercalates lithium. Suitable intercalation compounds for the anode include, for example, carbon compounds. The vanadium

20   oxide particles preferably have an average diameter from about 150 nm to about 5 nm. The separator element can include a polymer electrolyte or a porous polymeric material.

In another aspect, the invention features a

25   battery including an anode, an electrolyte, a cathode and a separator element disposed between the anode and the cathode, the electrolyte comprising lithium ions and the cathode comprising nanoparticles of intercalation type, electroactive material and a binder, wherein the

30   electroactive material in the cathode performs with an energy density greater than about 900 Wh/kg during discharge of the battery. The battery can be a secondary battery. The electroactive material of the cathode can have an energy density from about 950 Wh/kg

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to about 1200 Wh/kg. The electroactive material can include vanadium oxide. The electroactive material in the anode can include a lithium intercalation composition.

5   The present invention involves vanadium oxide nanoparticles that possess enhanced properties for selected applications due to the very small particle size and correspondingly large surface area. Vanadium oxide nanoparticles have been produced with a variety of
10   oxidation states and crystal structures. The particles generally have a narrow distribution of particle diameters. The particles can be produced using laser pyrolysis alone or combined with additional heating possibly in the presence of an oxidizing atmosphere.
15   Laser pyrolysis is a very versatile technique as applied herein for producing a variety of vanadium oxide nanoparticles, which can be subjected to further processing, if desired.

        In addition, the heat based processes
20   described herein provide valuable pathways to producing important vanadium oxide materials. The processes are efficient and low cost. The techniques are particularly valuable for producing nanoparticles. Vanadium oxide nanoparticles produced using the heat based processes
25   exhibit improved properties when incorporated into cathodes for lithium based batteries.

        Batteries based on nanoparticles such as vanadium oxide nanoparticles lead to lithium batteries and lithium ion batteries with improved performance
30   characteristics. In particular, the vanadium oxide nanoparticles have increased energy densities compared with larger diameter vanadium oxide particles. Using electroactive materials with increased energy densities yields batteries with higher capacities for a given

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amount of electroactive material. In this way, longer lasting, lighter and/or smaller batteries can be produced.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic illustration of the effect on surface area of a reduction in particle diameter.

Fig. 2 is a schematic, sectional view of an embodiment of a laser pyrolysis apparatus taken through the middle of the laser radiation path. The upper insert is a bottom view of the injection nozzle, and the lower insert is a top view of the collection nozzle.

Fig. 3 is a schematic, perspective view of a reaction chamber of an alternative embodiment of the laser pyrolysis apparatus, where the materials of the chamber are depicted as transparent to reveal the interior of the apparatus.

Fig. 4 is a sectional view of the reaction chamber of Fig. 3 taken along line 4-4.

Fig. 5 is a schematic, sectional view of an oven for heating vanadium oxide particles, in which the section is taken through the center of the quartz tube.

Fig. 6 is a schematic, perspective view of a battery of the invention.

Fig. 7 is a schematic, perspective view of the three electrode arrangement used in the examples.

Fig. 8 is an x-ray diffractogram of amorphous V_2O_5 nanoparticles.

Fig. 9 is an x-ray diffractogram of 2-D crystals of V_2O_5 nanoparticles.

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Fig. 10 is a transmission electron microscope view of amorphous V_2O_5 nanoparticles.

Fig. 11 is an x-ray diffractogram of crystalline VO_2 nanoparticles.

Fig. 12 is a transmission electron microscope view of crystalline VO_2 nanoparticles at lower magnification.

Fig. 13 is a transmission electron microscope view of crystalline VO_2 nanoparticles at higher magnification.

Fig. 14 is a plot depicting the distribution of particle sizes for the crystalline VO_2 nanoparticles depicted in Figs. 10 and 11.

Fig. 15 is an x-ray diffractogram of crystalline $VO_{1.27}$ nanoparticles.

Fig. 16 is an x-ray diffractogram of V_6O_{13} / VO_2 mixed phase nanoparticles.

Fig. 17 is an x-ray diffractogram of VO_2/V_2O_3 mixed phase nanoparticles.

Fig. 18 is an x-ray diffractogram of single phase crystalline V_2O_5 nanoparticles.

Fig. 19 is an x-ray diffractogram of single phase crystalline V_2O_5 nanoparticles produced using different starting materials than used to produce the particles which generated the diffractogram in Fig. 18.

Fig. 20 is an x-ray diffractogram of crystalline V_2O_5 nanoparticles made from VO_2 nanoparticles.

Fig. 21 is an x-ray diffractogram of VO_2 nanoparticles.

Fig. 22 is an x-ray diffractogram of crystalline V_2O_5 nanoparticles made with a flow rate of O_2 of 4.8 sccm.

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Fig. 23 is an x-ray diffractogram of crystalline V_2O_5 nanoparticles made with a flow rate of O_2 of 10.1 sccm.

Fig. 24 is an x-ray diffractogram of crystalline V_2O_5 nanoparticles made with a flow rate of O_2 of 20.9 sccm.

Fig. 25 is an x-ray diffractogram of mixed phase 2-D crystalline V_2O_5/VO_2 made from VO_2 nanoparticles.

Fig. 26 is an x-ray diffractogram of 2-D crystalline V_2O_5 made from amorphous V_2O_5.

Fig. 27 depicts the discharge/recharge cycling of a battery of the invention using VO_2 electroactive particles.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Vanadium oxide particles having diameters substantially less than a micron have been produced. Vanadium oxides nanoparticles have been made in a variety of oxidation states and with a variety of lattice structures. In particular, single phase crystalline nanoparticles have been demonstrated along with mixed phase nanoparticles and single phase amorphous nanoparticles.

To generate the desired nanoparticles, laser pyrolysis is used either alone or in combination with additional processing. Specifically, laser pyrolysis has been found to be a powerful technique for producing a variety of vanadium oxides nanoparticles. In addition, nanoscale vanadium oxide particles produced by laser pyrolysis can be subjected to heating in an oxygen environment or an inert environment to alter the properties (type) of vanadium oxide without destroying the nanoparticle size. These nanoscale vanadium oxide particles from laser pyrolysis provide useful starting

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material for further processing with heat. Therefore,
the combination of laser pyrolysis along with heat
processing provides the means to produce many forms of
vanadium oxide nanoparticles, with alternative routes of
5   production being available for, at least, some of the
vanadium oxide nanoparticles.

The small size of the particles results in a
significantly increased surface area for a given weight
of material. The increased surface area is depicted
10   graphically in Fig. 1., assuming spherical particles and
no aggregation.

The increased surface area of the
nanoparticles can be advantageous for certain
application. For example, cathodes for lithium based
15   batteries incorporating the vanadium oxide nanoparticles
exemplify improved performance, in particular, very high
energy densities.

The vanadium oxide nanoparticles not only have
high surface area resulting from their small size, but
20   they also can have a high degree of crystallinity. This
high degree of crystallinity generally is maintained
throughout each nanoparticle. Nanocrystalline materials
generally do not rely on pores to generate a high
surface area. Pores can be undesirable since they
25   represent a discontinuity in the crystalline lattice.
The surface area of the nanoparticles generally results
only from the faces of the particle.

A basic feature of successful application of
laser pyrolysis for the production of vanadium oxide
30   nanoparticles is production of a molecular stream
containing a vanadium precursor, a radiation absorber
and an oxygen source. The molecular stream is pyrolyzed
by an intense laser beam. The intense heat resulting
from the absorption of the laser radiation induces the

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oxidation of the vanadium precursor in the oxidizing environment. The laser pyrolysis provides for formation of phases of vanadium oxide that are difficult to form under thermodynamic equilibrium conditions. As the

5   molecular stream leaves the laser beam, the vanadium oxide particles are rapidly quenched.

A route for producing a variety of desirable vanadium oxide particles involves heating particles of an initial type of vanadium oxide to convert them to the

10   product particles. The heating step generally is performed in an oxidizing atmosphere, although for certain starting materials and corresponding products, an inert atmosphere generally is sufficient. Using these processing techniques, vanadium oxide particles

15   can be formed with a higher relative oxygen content and/or with a different crystal lattice relative to the starting material. The conversion results from heating at surprisingly low temperatures well below the melting point of the materials. With mild processing

20   temperatures, the particles generally do not significantly sinter.

These processes are especially desirable for the processing of nanoscale particles, i.e., particles having a diameter below a micron. Since the particles

25   do not significantly sinter, the nanoscale of the particles is preserved during the heat processing. Alternatively, the particles can be heated to slightly higher temperatures to sinter the particles in a controlled fashion to form somewhat larger particles, as

30   desired.

The vanadium oxide nanoparticles can be incorporated into a cathode film with a polymeric binder. The resulting film is appropriate for use as a cathode. While some of the vanadium oxides are

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reasonable electrical conductors, the film preferably incorporates additional electrically conductive particles held by the binder along with the vanadium oxide particles. The cathode film can be used in a
5   lithium battery or a lithium ion battery.

Appropriate vanadium oxide nanoparticles incorporated into a cathode for a lithium based battery exhibit a significantly increased energy density relative to comparable materials of larger particle
10 size. Amorphous nanoparticles can also be produced. Amorphous vanadium oxides can have very high energy densities. Amorphous bulk particles, however, can undergo crystalline rearrangements that reduce the energy density during the cycling of secondary
15 batteries.

Vanadium oxide nanoparticles produced by heat processing have been found to be especially useful for the production of lithium based batteries. In particular, when used as a cathode active material, the
20 vanadium oxide nanoparticles produced by heat processing have been found to yield very high energy densities. Crystalline V_2O_5 nanoparticles have an energy density for lithium based battery applications several times the theoretical maximum energy density values of
25 corresponding bulk (i.e., greater than micron sized) particles.

A.   Particle Production

Laser pyrolysis has been discovered to be a valuable tool for the production of nanoscale vanadium
30 oxide particles. In addition, the vanadium oxide nanoparticles produced by laser pyrolysis are a convenient material for further processing to expand the pathways for the production of certain vanadium oxide nanoparticles. Thus, using laser pyrolysis alone or in

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combination with additional processes, a wide variety of vanadium oxide nanoparticles can be produced. In some cases, alternative production pathways can be followed to produce comparable particles.

5   The reaction conditions determine the qualities of the vanadium oxide particles produced by laser pyrolysis. The appropriate reaction conditions to produce a certain type of nanoparticles generally depend on the design of the particular apparatus. The reaction
10   conditions for laser pyrolysis can be controlled relatively precisely in order to produce nanoparticles with desired properties. Specific conditions used to produce a variety of nanoparticles in a particular apparatus are described below in the examples.
15   Nevertheless, some general observations on the relationship between reaction conditions and the resulting nanoparticles can be made.

          Increasing the laser power results in increased reaction temperatures in the reaction region
20   as well as a faster quenching rate. A rapid quenching rate tends to favor production of VO_2. Similarly, increasing the chamber pressure also tends to favor the production of higher energy structures, such as VO_2. Also, increasing the concentration of oxygen source in
25   the reactant stream favors the production of vanadium oxides with increased amounts of oxygen, i.e., higher oxidation states of vanadium.

          Reactant gas flow rate and velocity of the reactant gas stream are inversely related to particle
30   size so that increasing the reactant gas flow rate or velocity tends to result in smaller particle size. Also, the growth dynamics of the particles have a significant influence on the size of the resulting particles. In other words, different crystal forms of

vanadium oxide have a tendency to form different size particles from other crystal forms under relatively similar conditions. Laser power also influences particle size with increased laser power favoring larger particle formation for lower melting materials and smaller particle formation for higher melting materials.

Appropriate precursor compounds generally include vanadium compounds with reasonable vapor pressures, i.e., vapor pressures sufficient to get desired amounts of precursor vapor in the reactant stream. The vessel holding the precursor compounds can be heated to increase the vapor pressure of the vanadium precursor, if desired. Suitable vanadium precursors include, for example, VCl_3, VCl_4, $VCCl$, $V(CO)_6$ and $VOCl_3$. The Cl in these representative precursor compounds can be replaced with other halogens, e.g., Br, I and F. Preferred oxygen sources include, for example, O_2, CO, CO_2, O_3 and mixtures thereof. The oxygen source should not react significantly with the vanadium precursor prior to entering the reaction zone since this generally would result in the formation of large particles.

Laser pyrolysis can be performed with a variety of optical laser frequencies. Preferred lasers operate in the infrared portion of the electromagnetic spectrum. CO_2 lasers are particularly preferred sources of laser light. Infrared absorbers for inclusion in the molecular stream include, for example, C_2H_4, NH_3, SF_6 and O_3. O_3 can act as both an infrared absorber and as an oxygen source. The radiation absorber, such as the infrared absorber, absorbs energy from the radiation beam and distributes the energy as heat to the other reactants to drive the pyrolysis.

Preferably, the energy absorbed from the radiation beam increases the temperature at a tremendous

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rate, many times the rate that energy generally would be produced even by strongly exothermic reactions under controlled condition. While the process generally involves nonequilibrium conditions, the temperature can
5   be described approximately based on the energy in the absorbing region. The laser pyrolysis process is qualitatively different from the process in a combustion reactor where an energy source initiates a reaction, but the reaction is driven by energy given off by an
10 exothermic reaction.

        An inert shielding gas can be used to reduce the amount of reactant and product molecules contacting the reactant chamber components. For the production of vanadium oxide nanoparticles, appropriate shielding
15 gases include, for example, Ar, He and N_2.

        An appropriate laser pyrolysis apparatus generally includes a reaction chamber isolated from the ambient environment. A reactant inlet connected to a reactant supply system produces a molecular stream
20 through the reaction chamber. A laser beam path intersects the molecular stream at a reaction zone. The molecular stream continues after the reaction zone to an outlet, where the molecular stream exits the reaction chamber and passes into a collection system. Generally,
25 the laser is located external to the reaction chamber, and the laser beam enters the reaction chamber through an appropriate window.

        Referring to Fig. 2, a particular embodiment 100 of a pyrolysis apparatus involves a reactant supply
30 system 102, reaction chamber 104, collection system 106 and laser 108. Reactant supply system 102 includes a source 120 of vanadium precursor. For liquid precursors, a carrier gas from carrier gas source 122 can be introduced into precursor source 120, containing

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liquid precursor to facilitate delivery of the precursor. The carrier gas from source 122 preferably is either an infrared absorber or an inert gas and is preferably bubbled through the liquid vanadium
5   precursor. The quantity of precursor vapor in the reaction zone is roughly proportional to the flow rate of the carrier gas.

Alternatively, carrier gas can be supplied directly from infrared absorber source 124 or inert gas
10   source 126, as appropriate. The oxidizing agent is supplied from source 128, which can be a gas cylinder. The gases from the vanadium precursor source 120 are mixed with gases from oxidizing agent source 128, infrared absorber source 124 and inert gas source 126 by
15   combining the gases in a single portion of tubing 130. The gases are combined a sufficient distance from reaction chamber 104 such that the gases become well mixed prior to their entrance into reaction chamber 104. The combined gas in tube 130 passes through a duct 132
20   into rectangular channel 134, which forms part of an injection nozzle for directing reactants into the reaction chamber 104.

Flow from sources 122, 124, 126 and 128 are preferably independently controlled by mass flow
25   controllers 136. Mass flow controllers 136 preferably provide a controlled flow rate from each respective source. Suitable mass flow controllers include, for example, Edwards Mass Flow Controller, Model 825 series, from Edwards High Vacuum International, Wilmington, MA.
30   Inert gas source 138 is connected to an inert gas duct 140, which flows into annular channel 142. A mass flow controller 144 regulates the flow of inert gas into inert gas duct 140. Inert gas source 126 can also

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function as the inert gas source for duct 140, if
desired.

5   The reaction chamber 104 includes a main
chamber 200. Reactant supply system 102 connects to the
main chamber 200 at injection nozzle 202. The end of
injection nozzle 202 has an annular opening 204 for the
passage of inert shielding gas, and a rectangular slit
206 for the passage of reactant gases to form a
molecular stream in the reaction chamber. Annular
10   opening 204 has, for example, a diameter of about 1.5
inches and a width along the radial direction of about
1/16 in. The flow of shielding gas through annular
opening 204 helps to prevent the spread of the reactant
gases and product particles throughout reaction chamber
15   104.

Tubular sections 208, 210 are located on
either side of injection nozzle 202. Tubular sections
208, 210 include ZnSe windows 212, 214, respectively.
Windows 212, 214 are about 1 inch in diameter. Windows
20   212, 214 are preferably plano-focusing lenses with a
focal length equal to the distance between the center of
the chamber to the surface of the lens to focus the beam
to a point just below the center of the nozzle opening.
Windows 212, 214 preferably have an antireflective
25   coating. Appropriate ZnSe lenses are available from
Janos Technology, Townshend, Vermont. Tubular sections
208, 210 provide for the displacement of windows 212,
214 away from main chamber 200 such that windows 212,
214 are less likely to be contaminated by reactants or
30   products. Window 212, 214 are displaced, for example,
about 3 cm from the edge of the main chamber 200.

Windows 212, 214 are sealed with a rubber o-
ring to tubular sections 208, 210 to prevent the flow of
ambient air into reaction chamber 104. Tubular inlets

216, 218 provide for the flow of shielding gas into tubular sections 208, 210 to reduce the contamination of windows 212, 214. Tubular inlets 216, 218 are connected to inert gas source 138 or to a separate inert gas source. In either case, flow to inlets 216, 218 preferably is controlled by a mass flow controller 220.

Laser 108 is aligned to generate a laser beam 222 that enters window 212 and exits window 214. Windows 212, 214 define a laser light path through main chamber 200 intersecting the flow of reactants at reaction zone 224. After exiting window 214, laser beam 222 strikes power meter 226, which also acts as a beam dump. An appropriate power meter is available from Coherent Inc., Santa Clara, CA. Laser 108 can be replaced with an intense conventional light source such as an arc lamp. Preferably, laser 108 is an infrared laser, especially a CW CO_2 laser such as an 1800 watt maximum power output laser available from PRC Corp., Landing, NJ or a Coherent® model 525 (Coherent, Inc., Santa Clara, CA) with a maximum power output of 375 watts.

Reactants passing through slit 206 in injection nozzle 202 initiate a molecular stream. The molecular stream passes through reaction zone 224, where reaction involving the vanadium precursor takes place. Heating of the gases in reaction zone 224 is extremely rapid, roughly on the order of $10^{5}°C/sec$ depending on the specific conditions. The reaction is rapidly quenched upon leaving reaction zone 224, and nanoparticles 228 are formed in the molecular stream. The nonequilibrium nature of the process allows for the production of nanoparticles with a highly uniform size distribution and structural homogeneity.

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The path of the molecular stream continues to
collection nozzle 230. Collection nozzle 230 is spaced
about 2 cm from injection nozzle 202. The small spacing
between injection nozzle 202 and collection nozzle 230
5   helps reduce the contamination of reaction chamber 104
with reactants and products. Collection nozzle 230 has
a circular opening 232. Circular opening 232 feeds into
collection system 106.

The chamber pressure is monitored with a
10   pressure gauge attached to the main chamber. The
chamber pressure generally ranges from about 5 Torr to
about 1000 Torr. The preferred chamber pressure for the
production of vanadium oxides ranges from about 80 Torr
to about 300 Torr.

15   Reaction chamber 104 has two additional
tubular sections not shown. One of the additional
tubular sections projects into the plane of the
sectional view in Fig. 2, and the second additional
tubular section projects out of the plane of the
20   sectional view in Fig. 2. When viewed from above, the
four tubular sections are distributed roughly,
symmetrically around the center of the chamber. These
additional tubular sections have windows for observing
the inside of the chamber. In this configuration of the
25   apparatus, the two additional tubular sections are not
used to facilitate production of nanoparticles.

Collection system 106 can include a curved
channel 250 leading from collection nozzle 230. Because
of the buoyant nature of the nanoparticles, the product
30   nanoparticles follow the flow of the gas around curves.
Collection system 106 includes a filter 252 within the
gas flow to collect the product nanoparticles. A
variety of materials such as teflon, glass fibers and
the like can be used for the filter as long as the

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material is inert and has a fine enough mesh to trap the
particles. Preferred materials for the filter include,
for example, a glass fiber filter from ACE Glass Inc.,
Vineland, NJ.

5   Pump 254 is used to maintain collection system
106 at a reduced pressure. A variety of different pumps
can be used. Appropriate pumps 254 include, for
example, Busch Model B0024 pump from Busch, Inc.,
Virginia Beach, VA with a pumping capacity of about 25
10 cubic feet per minute (cfm) and Leybold Model SV300 pump
from Leybold Vacuum Products, Export, PA with a pumping
capacity of about 195 cfm. It may be desirable to flow
the exhaust of the pump through a scrubber 256 to remove
any remaining reactive chemicals before venting into the
15 atmosphere. The entire apparatus 100 can be placed in
a fume hood for ventilation purposes and for safety
considerations. Generally, the laser remains outside of
the fume hood because of its large size.

The apparatus is controlled by a computer.
20 Generally, the computer controls the laser and monitors
the pressure in the reaction chamber. The computer can
be used to control the flow of reactants and/or the
shielding gas. The pumping rate is controlled by either
a manual needle valve or an automatic throttle valve
25 inserted between pump 254 and filter 252. As the
chamber pressure increases due to the accumulation of
particles on filter 252, the manual valve or the
throttle valve can be adjusted to maintain the pumping
rate and the corresponding chamber pressure.

30   The reaction can be continued until sufficient
nanoparticles are collected on filter 252 such that the
pump can no longer maintain the desired pressure in the
reaction chamber 104 against the resistance through
filter 252. When the pressure in reaction chamber 104

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can no longer be maintained at the desired value, the
reaction is stopped, and the filter 252 is removed.
With this embodiment, about 3-5 grams of nanoparticles
can be collected in a single run before the chamber
5   pressure can no longer be maintained. A single run
generally can last from about 10 minutes to about 1 hour
depending on the type of particle being produced and the
particular filter. Therefore, it is straightforward to
produce a macroscopic quantity of nanoparticles, i.e.,
10   a quantity visible with the naked eye.

     The reaction conditions can be controlled
relatively precisely. The mass flow controllers are
quite accurate. The laser generally has about 0.5
percent power stability. With either a manual control
15   or a throttle valve, the chamber pressure can be
controlled to within about 1 percent.

     The configuration of the reactant supply
system 102 and the collection system 106 can be
reversed. In this alternative configuration, the
20   reactants are supplied from the bottom of the reaction
chamber, and the product particles are collected from
the top of the chamber. This alternative configuration
tends to result in a slightly higher collection of
product since vanadium oxide nanoparticles tend to be
25   buoyant in the surrounding gases. In this
configuration, it is preferable to include a curved
section in the collection system so that the collection
filter is not mounted directly above the reaction
chamber.

30   An alternative design of a laser pyrolysis
apparatus has been described. See, commonly assigned
U.S. Patent Application No. 08/808,850, entitled
"Efficient Production of Particles by Chemical
Reaction," incorporated herein by reference. This

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alternative design is intended to facilitate production of commercial quantities of nanoparticles. A variety of configurations are described for injecting the reactant materials into the reaction chamber.

5   The alternative apparatus includes a reaction chamber designed to minimize contamination of the walls of the chamber with particles, to increase the production capacity and to make efficient use of resources. To accomplish these objectives, the reaction
10   chamber conforms generally to the shape of an elongated reactant inlet, decreasing the dead volume outside of the molecular stream. Gases can accumulate in the dead volume, increasing the amount of wasted radiation through scattering or absorption by nonreacting
15   molecules. Also, due to reduced gas flow in the dead volume, particles can accumulate in the dead volume causing chamber contamination.

        The design of the improved reaction chamber 300 is schematically shown in Figs. 3 and 4. A reactant
20   gas channel 302 is located within block 304. Facets 306 of block 304 form a portion of conduits 308. Another portion of conduits 308 join at edge 310 with an inner surface of main chamber 312. Conduits 308 terminate at shielding gas inlets 314. Block 304 can be repositioned
25   or replaced, depending on the reaction and desired conditions, to vary the relationship between the elongated reactant inlet 316 and shielding gas inlets 314. The shielding gases from shielding gas inlets 314 form blankets around the molecular stream originating
30   from reactant inlet 316.

        The dimensions of elongated reactant inlet 316 preferably are designed for high efficiency particle production. Reasonable dimensions for the reactant inlet for the production of vanadium oxide nanoparticle,

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when used with a 1800 watt CO_2 laser, are from about 5 mm to about 1 meter.

Main chamber 312 conforms generally to the shape of elongated reactant inlet 316. Main chamber 312 includes an outlet 318 along the molecular stream for removal of particulate products, any unreacted gases and inert gases. Tubular sections 320, 322 extend from the main chamber 312. Tubular sections 320, 322 hold windows 324, 326 to define a laser beam path 328 through the reaction chamber 300. Tubular sections 320, 322 can include shielding gas inlets 330, 332 for the introduction of shielding gas into tubular sections 320, 322.

The improved apparatus includes a collection system to remove the nanoparticles from the molecular stream. The collection system can be designed to collect a large quantity of particles without terminating production or, preferably, to run in continuous production by switching between different particle collectors within the collection system. The collection system can include curved components within the flow path similar to curved portion of the collection system shown in Fig. 2. The configuration of the reactant injection components and the collection system can be reversed such that the particles are collected at the top of the apparatus.

As noted above, properties of the vanadium oxide particles can be modified by further processing. The starting material for the heat treatment can be any type of solid vanadium oxide compound. Suitable materials include, for example, VO, $VO_{1.27}$, VO_2, V_2O_3, V_3O_5 and amorphous V_2O_5. The starting materials generally can be particles of any size and shape. In addition, particles used as starting material can have been

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subjected to one or more prior heating steps under different conditions.

Nanoscale particles are preferred starting materials. The nanoscale particles have an average
5   diameter of less than about 1000 nm and preferably from about 500 nm to about 5 nm, and more preferably from about 150 nm to about 5 nm. Suitable nanoscale starting materials have been produced by laser pyrolysis. The heat processing can be performed on initial particles
10   that were not produced by laser pyrolysis, including particles that do not have a generally spherical shape, i.e., particles that are flat sheets or needle like.

The vanadium oxide particles are preferably heated in an oven or the like to provide generally
15   uniform heating. The processing conditions generally are mild. The temperature of heating is low relative to the melting point of both the starting material and the product material. The temperature generally is at least 300°C below the melting point and preferably at least
20   450°C below the melting point of either the starting material or the product material. For nanoparticles, the processing temperature generally ranges from about 50°C to about 500°C, and more preferably from about 60°C to about 400°C. For bulk particles, the temperature
25   ranges from about 80°C to about 1000°C and more preferably from about 100°C to about 800°C.

The heating preferably is continued for more than about 1 hour, and generally is continued for from about 2 hours to about 100 hours, preferably from about
30   10 hours to about 50 hours. For certain target product particles, additional heating does not lead to further variation in the particle composition. The atmosphere for the heating process generally is an oxidizing atmosphere. For conversion of amorphous particles to

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crystalline particles or from one crystalline structure to a different crystalline structure of essentially the same stoichiometry, the atmosphere generally can be inert. The atmosphere over the particles can be static, or gases can be flowed through the system.

Appropriate oxidizing gases include, for example, O_2, O_3, CO, CO_2, and combinations thereof. Oxidizing gases optionally can be mixed with inert gases such as Ar, He and N_2. When inert gas is mixed with the oxidizing gas, the gas mixture can be from about 1 percent oxidizing gas to about 99 percent oxidizing gas, and more preferably from about 5 percent oxidizing gas to about 99 percent oxidizing gas. Alternatively, either essentially pure oxidizing gas or pure inert gas can be used, as desired.

The precise conditions can be altered to vary the type of vanadium oxide product produced. For example, the temperature, time of heating, heating and cooling rates, the gases and the exposure conditions with respect to the gases can all be changed, as desired. Generally, while heating under an oxidizing atmosphere, the longer the heating period the more oxygen that is incorporated into the material, prior to reaching equilibrium. Once equilibrium conditions are reached, the overall conditions determine the crystalline phase of the powders.

A variety of ovens can be used to perform the heating. An example of an apparatus 400 to perform this processing is displayed in Fig. 5. Apparatus 400 includes a tube 402 into which the particles are placed. Tube 402 generally is connected to an oxidizing gas source 404 and inert gas source 406. Oxidizing gas, inert gas or a combination thereof to produce the

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desired atmosphere are placed within tube 402 from the appropriate gas source(s).

Preferably, the desired gases are flowed through tube 402. Various flow rates can be used. The flow rate preferably is between about 1 standard cubic centimeters per minute (sccm) to about 1000 sccm and more preferably from about 10 sccm to about 500 sccm. The flow rate generally is constant through the processing step, although the flow rate and the composition of the gas can be varied systematically over time during processing, if desired. Alternatively, a static gas atmosphere can be used.

Tube 402 is located within oven or furnace 408. Oven 408 can be adapted from a commercial furnace such as Mini-Mite™ 1100°C Tube Furnace from Revco/Lindberg, Asheville, NC. Oven 408 maintains the relevant portions of the tube at a relatively constant temperature, although the temperature can be varied systematically through the processing step, if desired. Temperature in oven 408 generally is measured with a thermocouple 410.

The vanadium oxide particles can be placed in tube 402 within a vial 412. Vial 412 prevents loss of the particles due to gas flow. Vial 412 generally is oriented with the open end directed toward the direction of the source of the gas flow. Alternatively, the particles could be placed within a material that would permit gas flow while holding the particles in place. For example, the collection filter from the laser pyrolysis could be placed within the tube in an orientation that would tend to keep the particles on the filter material.

The precise conditions including the type of oxidizing gas (if any), concentration of oxidizing gas,

pressure or flow rate of gas, temperature and processing time can be selected to produce the desired type of product material.

High melting point VO_2 is relatively easy to form in the laser pyrolysis apparatuses described above. VO_2 is a suitable starting product for oxidation to other forms of vanadium oxide. Some empirical adjustment may be required to produce the conditions appropriate to generate a desired material.

B.   Properties of Vanadium Oxide Particles

Vanadium oxide has an intricate phase diagram due to the many possible oxidation states of vanadium. Vanadium is known to exist in oxidation states between V^{+5} and V^{+2}. The energy differences between the oxides of vanadium in the different oxidation states is not large.   Therefore,   it   is   possible   to   produce stoichiometric mixed valence compounds. Known forms of vanadium oxide include VO, $VO_{1.27}$, V_2O_3, V_3O_5, VO_2, V_6O_{13}, V_4O_9, V_3O_7, and V_2O_5. The present processing approaches successfully yield single phase vanadium oxide in many different oxidation states, as evidenced by x-ray diffraction studies. These single phase materials are generally   crystalline,   although   some   amorphous nanoparticles have been produced. The present heat treatment   approach   is   useful   for   increasing   the oxidation state of vanadium oxide particles or for converting vanadium oxide particles to more ordered phases.

There are also mixed phase regions of the vanadium oxide phase diagram. In the mixed phase regions, particles can be formed that have domains with different oxidation states, or different particles can be simultaneously formed with vanadium in different oxidation states. In other words, certain particles or

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portions of particles have one stoichiometry while other
particles or portions of particles have a different
stoichiometry. Mixed phase nanoparticles have been
formed as described below. Non-stoichiometric materials
5   also can be formed.

The vanadium oxides generally form crystals
with octahedral or distorted octahedral coordination.
Specifically, VO, V_2O_3, VO_2, V_6O_{13} and V_3O_7 can form
crystals with octahedral coordination. In addition,
10   V_3O_7 can form crystals with trigonal bipyramidal
coordination. V_2O_5 forms crystals with square pyramidal
or distorted octahedral coordination. V_2O_5 recently
also has been produced in a two dimensional crystal
structure. See, M. Hibino, et al., Solid State Ionics
15   79:239-244 (1995), incorporated herein by reference.
When produced under appropriate conditions, the vanadium
oxide nanoparticles can be amorphous. The crystalline
lattice of the vanadium oxide can be evaluated using x-
ray diffraction measurements.

20   With heat processing, an increase in the
oxidation state of vanadium within a vanadium oxide
particles is generally accomplished within an oxidizing
atmosphere. The conversion of a vanadium oxide to a
more ordered crystalline lattice with the same
25   stoichiometry generally can be accomplished with an
oxidizing atmosphere or an inert atmosphere.

A collection of vanadium oxide nanoparticles
has an average diameter of less than a micron,
preferably from about 5 nm to about 500 nm and more
30   preferably from about 5 nm to about 150 nm, and even
more preferably from about 10 nm to about 50 nm. The
nanoparticles generally have a roughly spherical gross
appearance. Upon closer examination, the particles
generally have facets corresponding to the underlying

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crystal lattice. Nevertheless, the nanoparticles tend
to exhibit growth that is roughly equal in the three
physical dimensions to give a gross spherical
appearance. Diameter measurements on particles with
asymmetries are based on an average of length
measurements along the principle axes of the particle.
The measurements along the principle axes preferably are
each less than about 1 micron for at least about 95
percent of the nanoparticles, and more preferably for at
least about 98 percent of the nanoparticles.

Because of their small size, the nanoparticles
tend to form loose agglomerates due to van der Waals
forces between nearby particles. Nevertheless, the
nanometer scale of the particles is clearly observable
in transmission electron micrographs of the particles.
For crystalline nanoparticles, the particle size
generally corresponds to the crystal size. The
particles generally have a surface area corresponding to
particles on a nanometer scale as observed in the
micrographs. Furthermore, the particles manifest unique
properties due to their small size and large surface
area per weight of material, as described herein with
respect to use of vanadium oxide nanoparticles in
lithium based batteries.

The nanoparticles preferably have a high
degree of uniformity in size. As determined from
examination of transmission electron micrographs, the
particles generally have a distribution in sizes such
that at least about 95 percent of the particles have a
diameter greater than about 40 percent of the average
diameter and less than about 160 percent of the average
diameter. Preferably, the nanoparticles have a
distribution of diameters such that at least about 95
percent of the particles have a diameter greater than

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about 60 percent of the average diameter and less than about 140 percent of the average diameter. In addition, the nanoparticles generally have a very high purity level. Vanadium oxide nanoparticles are expected to

5   have a purity greater than the reactant gases because the crystal formation process tends to exclude contaminants from the lattice.

The above described techniques have been successfully applied to the production of nanoparticles

10   of vanadium oxide with several different stoichiometries and with different crystal structures with the same stoichiometry. The structures and compositions have been examined using x-ray defractometry. The sizes of some of the particles have been examined using

15   transmission electron microscopy. The properties of the types of vanadium oxide nanoparticles obtained are summarized in Table 1.

Table 1

20

Stoichiometry	Lattice
Single Phase VO_2	Monoclinic
Single Phase $VO_{1.27}$	Tetragonal
Single Phase V_2O_5	Amorphous 2-D crystals Crystalline
Mixed Phase V_6O_{13} + VO_2	V_6O_{13} majority/Monoclinic
Mixed Phase V_2O_5 + VO_2	V_2O_5 majority/Rhombohedral

C.   Lithium Based Batteries

Referring to Fig. 6, battery 450 has an anode

30   452, a cathode 454 and separator 456 between anode 452 and cathode 454. A single battery can include multiple cathodes and/or anodes. Electrolyte can be supplied in a variety of ways as described further below. Battery 450 preferably includes current collectors 458, 460

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associated with anode 452 and cathode 454, respectively. Multiple current collectors can be associated with each electrode if desired.

5   Lithium has been used in reduction/oxidation reactions in batteries because they are the lightest metal and because they are the most electropositive metal. Certain forms of vanadium oxide are known to incorporate lithium ions into its structure through intercalation or similar mechanisms such as topochemical

10   absorption. Intercalation of lithium ions into suitable forms of a vanadium oxide lattice forms Li_xVO_y. Appropriate vanadium oxides can be an effective electroactive material for a cathode in either a lithium or lithium ion battery.

15   Lithium intercalated vanadium oxide is formed in the battery during discharge. The lithium leaves the lattice upon recharging, i.e., when a voltage is applied to the cell such that electric current flows into the cathode due to the application of an external EMF to the

20   battery. Intercalation generally is reversible, making certain vanadium oxides suitable for the production of secondary batteries.

Cathode 454 includes electroactive nanoparticles such as vanadium oxide nanoparticles held

25   together with a binder such as a polymeric binder. Nanoparticles for use in cathode 454 generally can have any shape, e.g., roughly spherical nanoparticles or elongated nanoparticles. Cathode 454 can include other electroactive nanoparticles such as TiO_2 nanoparticles.

30   The production of TiO_2 nanoparticles has been described, see U.S. Patent Ser. No. 4,705,762, incorporated herein by reference. TiO_2 nanoparticles are expected to exhibit relatively high energy densities in lithium

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based batteries by analogy with the results discovered
for vanadium oxides nanoparticles.

While some of the electroactive materials,
such as certain vanadium oxides, are reasonable
electrical conductors, the cathode optionally can
include electrically conductive particles in addition to
the electroactive nanoparticles. These supplementary,
electrically conductive particles generally are also
held by the binder. Suitable electrically conductive
particles include conductive carbon particles such as
carbon black, metal particles such as silver particles
and the like.

With vanadium oxide nanoparticles, very high
energy densities have been achieved. Preferred vanadium
oxide nanoparticles have energy densities in lithium
based batteries significantly greater than the
theoretical maximum values for the corresponding bulk
vanadium oxide particles. Vanadium oxide nanoparticles
preferably have energy densities at least about 150
percent of the theoretical maximum of the bulk material,
and more preferably at least about 200 percent of the
theoretical maximum of the bulk material. Specifically,
preferred vanadium oxide nanoparticles in lithium based
batteries have an energy density of at least about 900
Wh/kg, preferably at least about 1000 Wh/kg.
Electroactive nanoparticles can have an energy density
in the range from 1000 Wh/kg to about 1200 Wh/kg.

High loadings of particles can be achieved in
the binder. Particles preferably make up greater than
about 80 percent by weight of the cathode, and more
preferably greater than about 90 percent by weight. The
binder can be any of various suitable polymers such as
polyvinylidene fluoride, polyethylene oxide,

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polyethylene, polypropylene, polytetrafluoroethylene, polyacrylates and mixtures and copolymers thereof.

Anode 452 can be constructed from a variety of materials that are suitable for use with lithium ion electrolytes. In the case of lithium batteries, the anode can include lithium metal or lithium alloy metal either in the form of a foil, grid or metal particles in a binder.

Lithium ion batteries use particles of an composition that can intercalate lithium. The particles are held with a binder in the anode. Suitable intercalation compounds include, for example, graphite, synthetic graphite, coke, mesocarbons, doped carbons, fullerenes, niobium pentoxide and SnO_2.

Current collectors 458, 460 facilitate flow of electricity from battery 450. Current collectors 458, 460 are electrically conductive and generally made of metal such as nickel, iron, stainless steel, aluminum and copper and can be metal foil or preferably a metal grid. Current collector 458, 460 can be on the surface of their associated electrode or embedded within their associated electrode.

The separator element 456 is electrically insulating and provides for passage of at least some types of ions. Ionic transmission through the separator provides for electrical neutrality in the different sections of the cell. The separator generally prevents electroactive compounds in the cathode from contacting electroactive compounds in the anode.

A variety of materials can be used for the separator. For example, the separator can be formed from glass fibers that form a porous matrix. Preferred separators are formed from polymers such as those suitable for use as binders. Polymer separators can be

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porous to provide for ionic conduction. Alternatively, polymer separators can be solid electrolytes formed from polymers such as polyethylene oxide. Solid electrolytes incorporate electrolyte into the polymer matrix to
5   provide for ionic conduction without the need for liquid solvent.

Electrolytes for lithium batteries or lithium ion batteries can include any of a variety of lithium salts. Preferred lithium salts have inert anions and
10   are nontoxic. Suitable lithium salts include, for example, lithium hexafluorophosphate, lithium hexafluoroarsenate, lithium bis(trifluoromethyl sulfonyl imide), lithium trifluoromethane sulfonate, lithium tris(trifluoromethyl sulfonyl) methide, lithium
15   tetrafluoroborate, lithium perchlorate, lithium tetrachloroaluminate, lithium chloride and lithium perfluorobutane.

If a liquid solvent is used to dissolve the electrolyte, the solvent preferably is inert and does
20   not dissolve the electroactive materials. Generally appropriate solvents include, for example, propylene carbonate, dimethyl carbonate, diethyl carbonate, 2-methyl tetrahydrofuran, dioxolane, tetrahydrofuran, 1, 2-dimethoxyethane, ethylene carbonate, γ-butyrolactone,
25   dimethyl sulfoxide, acetonitrile, formamide, dimethylformamide and nitromethane.

The shape of the battery components can be adjusted to be suitable for the desired final product, for example, a coin battery, a rectangular construction
30   or a cylindrical battery. The battery generally includes a casing with appropriate portions in electrical contact with current collectors and/or electrodes of the battery. If a liquid electrolyte is used, the casing should prevent the leakage of the

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electrolyte. The casing can help to maintain the battery elements in close proximity to each other to reduce resistance within the battery. A plurality of battery cells can be placed in a single case with the

5   cells connected either in series or in parallel.

                              Examples
              These examples demonstrate the production of nanoscale vanadium oxides with various lattices and

10   stoichiometry. The particles described in Examples 1-5 were produced using essentially the apparatus of Fig. 2 described above. The heat treatments described in the Examples were preformed in an oven essentially as described above with respect to Fig. 5. Between about

15   100 and about 300 mg of nanoparticles were placed within an open 1 cc vial within the tube in the oven. The specific conditions for heat processing are described in the examples below.
              In addition, vanadium oxide based lithium

20   batteries were evaluated to determine the charge capacity and energy density of the vanadium oxide powders used as active materials in the cathodes. The batteries tested in the following examples were all produced following a common procedure. The vanadium

25   oxide powders (VO) were mixed with a conductive acetylene black powder (AB) (Catalog number 55, Chevron Corp.) at a ratio of 60:30. The powder mixture was ground with a mortar and palette to thoroughly mix the powders.

30   A few drops of polyvinylidene fluoride (PVDF) solution were added to the homogeneous powder mixture. The 10 percent PVDF solution included PVDF (Catalog reference R-1, Elf Atochem North America, Inc., Philadelphia, PA) dissolved in 1-methyl-2-pyrroidinone

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(Aldrich Chemical Co., Milwaukee, WI). The final ratio of VO:AB:PVDF was 60:30:10. The resulting slurry was spread onto a preweighed nickel metal mesh. The mesh with the slurry was baked in a vacuum oven overnight at 120°C to remove the solvent and residual moisture. After removal from the oven, the electrodes were immediately placed in a glove box (Vacuum Atmosphere Co., Hawthorne, CA) under an argon atmosphere and weighted again.

All discharge/charge experiments were conducted in the glove box. The water and oxygen concentrations in the glove box were measured to be less than 1 ppm and 1.5 ppm, respectively. The samples were tested in a three electrode configuration, as shown in Fig. 7. In the test set up, cathode 502 on nickel mesh 504 is place in container 506. Container 506 holds liquid electrolyte 508. Counter electrode 510 and reference electrode 512 are also placed into container 506. Lithium metal was used as both counter electrode and reference electrode. The electrodes are connected to a battery testing system 514.

No separator is needed for this testing configuration since the electrodes are physically separated. Alternatively, the liquid electrolyte can be viewed as the separator. The liquid electrolyte (from Merck & Co., Inc.) was 1M $LiClO_4$ in propylene carbonate.

The samples were tested at the same discharge/charge rate of C/20 (i.e., a rate such that the cathode would be fully discharged in 20 hours), and cycled between 4.0 volts and 1.8 volts at 25°C. The measurements were controlled by an Arbin Battery Testing System, Model BT4023, from Arbin Instruments, College Station, TX. The charging/discharging profiles were

recorded, and the discharge capacity and energy density of the active materials were obtained.

The energy density is evaluated by the integral over the discharge time of the voltage
5 multiplied by the current divided by the mass of the active material. The current is kept approximately constant during discharge. Currents used during testing ranged from about 0.08 mA to about 0.12 mA. The current is adjusted to have an approximately constant current
10 density for all the tests. The current density was about 0.1 mA/cm². The active material mass ranged from about 5 to about 17 mg.

Example 1 - Single phase V_2O_5 - Laser Pyrolysis

The synthesis of V_2O_5 described in this
15 example was performed by laser pyrolysis. The $VOCl_3$ (Strem Chemical, Inc., Newburyport, MA) precursor vapor is carried into the reaction chamber by bubbling Ar gas through the $VOCl_3$ liquid stored in a container at room temperature. The reactant gas mixture containing $VOCl_3$,
20 Ar, O_2 and C_2H_4 is introduced into the reactant gas nozzle for injection into the reactant chamber. The reactant gas nozzle had an opening with dimensions as specified in Table 2. C_2H_4 gas acts as a laser absorbing gas. Argon was used as an inert gas.
25 The synthesized vanadium oxide nanoscale particles can be directly handled in the air. The production rate was typically about 5 - 10 g/hour of nanoparticles. The samples were subsequently examined by transmission electron microscopy (TEM) to determine
30 particle sizes and by x-ray diffraction to evaluate the composition and structure.

Using laser pyrolysis, both amorphous V_2O_5 and 2-D crystalline V_2O_5 have been produced. Representative

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reaction conditions used to produce these particles are described in the following table.

TABLE 2

Phase	V_2O_5	V_2O_5	V_2O_5	V_2O_5
Crystal Structure	Amorphous	Amorphous	Amorphous	2D Crystal
Battery Capacity (mAh/g)	182			146
Pressure (Torr)	135	142.5	110	300
Argon - Win. (sccm)	700	700	700	700
Argon - Sld. (slm)	0.98	0.98	2.1	1.12
Ethylene (sccm)	603	1072	173	268
Carrier Gas (sccm)	116 (Ar)	676 (Ar)	140 (Ar)	676 (Ar)
Oxygen (sccm)	284	642	88	400
Laser Output (watts)	180	215	150	67
Nozzle Size	5/8" x 1/16"	5/8" x 1/16"	5/8" x 1/8"	5/8" x 1/16"

sccm = standard cubic centimeters per minute

slm = standard liters per minute

Argon - Win. = argon flow through inlets 216,218

Argon - Sld. = argon flow through annular channel 142

Representative x-ray diffractograms for amorphous V_2O_5 and 2-D V_2O_5 are shown in Figs. 8 and 9, respectively. The x-ray diffractograms were obtained using Cu(Ka) radiation line on a Siemens D500 x-ray diffractometer. Referring to Fig. 8, the broad peaks centered around 2θ ~ 28 degrees and 58 degrees are typical of amorphous phase of vanadium oxide. See, U.S. Patent No. 4,675,260. The amorphous nature of the sample is confirmed by transmission electron microscopy examination as shown in Fig. 10. The TEM micrograph shows a material that has disordered atomic arrangement.

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The diffractogram in Fig. 9 corresponds to a recently reported 2-D crystal structure for V_2O_5. See, x-ray diffractogram in Fig. 2 of Hibino et al., above. The materials described by Hibino et al. had been made using liquid phase reactions.

Example 2 - Single Phase VO₂

These particles were produced using a similar laser pyrolysis set up as described in Example 1. The reactant gas nozzle had dimensions 5/8 in x 1/16 in. For the production of VO_2, C_2H_4 was bubbled through the $VOCl_3$ liquid precursor at room temperature. Representative reaction conditions for the production of this material are described in Table 3.

Table 3

Phase	VO_2	VO_2	$VO_{1.27}$
Crystal Structure	Monoclinic	Monoclinic	Tetragonal
Battery Capacity (mAh/g)	249		118.4
Pressure (Torr)	320	127	200
Argon-Win (sccm)	700	700	700
Argon-Sld. (slm)	5.6	0.98	2.8
Ethylene (sccm)	460	268	402
Carrier Gas (sccm)	460(Ethyl.)	676(Ar)	402(Ethyl.)
Oxygen (sccm)	36	200	196
Laser Output (watts)	96	220	100

An x-ray diffractogram of representative product nanoparticles is shown in Fig. 11. Clear diffraction peaks corresponding to a monoclinic crystalline structure are visible. The identified structure from the diffractogram is almost identical to that of the corresponding bulk material, which has

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larger particle sizes.   Therefore, the novel
nanoparticle materials have distinct properties while
maintaining the same crystalline lattice of the bulk
material.

5   TEM photos at both high and low magnifications
were obtained of representative nanoparticles with
similar x-ray diffraction patterns, as shown in Figs. 12
and 13. An approximate size distribution was determined
by manually measuring diameters of the particles shown

10   in Fig. 12. The distribution of diameters is shown in
Fig. 14. An average particle size of about 22 nm was
obtained. Only those particles showing clear particle
boundaries were measured and recorded to avoid regions
of distorted in the micrograph. This should not bias

15   the measurements obtained since the single view of the
micrograph may not show a clear view of all particles
because of the orientation of the crystals. It is
significant that the particles span a rather narrow
range of sizes. In this case, the largest to the

20   smallest particles differ by no more than about 15 nm.
Crystallinity of the particles is confirmed in Fig. 13
where the underlying lattice structure is visible.

Example 3 - Single Phase $VO_{1.27}$

          The experimental arrangement for the

25   production of $VO_{1.27}$ is the same as that described in
Example 2. Representative conditions used to produce
these particles are given in Table 3, above.

          The x-ray diffractogram for this material is
shown in Fig. 15, and is characteristic of crystalline

30   $VO_{1.27}$ material.

Example 4 - V_6O_{13}/VO_2 Mixed Phase Material

          The experimental configuration was the same as
described with respect to Example 1. The reactant gas

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nozzle had dimensions 5/8 in x 1/8 in. The particular experimental parameters are given in Table 4.

Table 4

Phase	V_6O_{13} + VO_2	V_6O_{13} + VO_2	VO_2 + V_2O_3
Crystal Structure	Monoclinic	Monoclinic	
Pressure (Torr)	110	110	410
Argon - Win (sccm)	700	700	700
Argon - Sld. (slm)	2.1	2.1	11.2
Ethylene (sccm)	173	209	460
Carrier Gas (sccm)	140(Ar)	140(Ar)	Ethylene
Oxygen (sccm)	88	88	36
Laser Output (watts)	192	100	90

A characteristic x-ray diffractogram of the nanoparticles is shown in Fig. 16. The diffractogram contains a combination of peaks identifiable with both crystalline V_6O_{13} and crystalline VO_2. Both types of crystals are monoclinic. The V_6O_{13} phase is the majority phase. Appropriate reaction conditions should yield single phase V_6O_{13}.

Example 5 - VO_2/V_2O_3 Mixed Phase Material

The experimental configuration was the same as described with respect to Example 4. The reactant gas nozzle had dimensions 5/8 in x 1/16 in. Representative experimental parameters to produce these particles are given in Table 4, above. The x-ray diffractogram is shown in Fig. 17. The diffractogram contains a combination of peaks identifiable with both crystalline VO_2 and crystalline V_2O_3. Note that the conditions for the production of these particles involves a reduced amount of O_2 relative to the other gases in the reactant stream.

Example 6 - Crystalline V_2O_5 - Oven Processed

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A first sample of crystalline V_2O_5 was produced from amorphous V_2O_5 by baking the amorphous particles in an oven for 16.0 hours. The amorphous V_2O_5 starting material was produced by laser pyrolysis according to the parameters in the second column of Table 2. The oven was set at a temperature of 202°C. Oxygen gas flowed through a 1.0 in. diameter quartz tube at a flow rate of 105.6 sccm. Between about 100 and about 300 mg of nanoparticles were placed within an open 1 cc vial within the tube in the oven. The resulting nanoparticles were single phase crystalline V_2O_5 nanoparticles. The corresponding x-ray diffractogram is presented in Fig. 18. The x-ray diffractogram is characteristic of orthorhombic V_2O_5.

A second sample of crystalline V_2O_5 were made from crystalline VO_2 using the same starting materials. The starting materials were crystalline VO_2 nanoparticles produced by laser pyrolysis using the conditions specified in the second column of Table 3. The second sample was treated in an oven under the same conditions as the first sample.

The resulting nanoparticles for the second sample were single phase V_2O_5. These had a smaller average diameter than the particles from the first sample because of the smaller size of the starting nanoparticles used to produce the second sample. An x-ray diffractogram for the second sample is shown in Fig. 19.

Example 7 - Orthorhombic V_2O_5 from VO_2 Nanoparticles

The starting materials for the heat treatment were VO_2 nanoparticles produced by laser pyrolysis according to the parameters in the second column of Table 3. An x-ray diffractogram of the VO_2

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nanoparticles is essentially the same as the x-ray diffractogram in Fig. 11.

   The nanoparticles were heat treated at a temperature of 202°C with oxygen gas flowed through a 1
5 inch tube at a rate of 105.6 sccm. The heat treatment was continued for about 16 hours. The resulting nanoparticles were single phase crystalline V_2O_5 nanoparticles. The x-ray diffractogram of this material is shown in Fig. 20. From the x-ray diffractogram, it
10 could be determined that the resulting particles were orthorhombic V_2O_5.

   Additional samples of crystalline V_2O_5 were made from nanoparticles of crystalline VO_2. The laser pyrolysis conditions to produce the VO_2 nanoparticles
15 are presented in Table 5.

Table 5

Phase	VO_2
Crystal Structure	Monoclinic
Pressure (Torr)	100
Argon F.R. - Win (sccm)	700
Argon F.R. - Sld. (slm)	5.6
Ethylene (sccm)	311
Carrier Gas (sccm)	311(ethyl.)
Oxygen (sccm)	84
Laser Output (watts)	102
Nozzle Size	5/8" x 1/16"

   sccm = standard cubic centimeters per minute
30 slm = standard liters per minute
   Argon - Win. = argon flow through inlets 216, 218
   Argon - Sld. = argon flow through annular channel 142

   The x-ray diffractogram for the VO_2 nanoparticles is shown in Fig. 21. Three sample of the
35 VO_2 nanoparticles were subjected to heat treatment. All

three samples were treated for 17 hours in the 1 inch
quartz tube with an flow of inert gas (Ar) of 103 sccm.
Samples 1, 2 and 3, in addition, had O_2 flow rates of
4.8 sccm, 10.1 sccm and 20.9 sccm, respectively.

30   slm = standard liters per minute
        Argon - Win. = argon flow through inlets 216, 218
        Argon - Sld. = argon flow through annular channel 142
               The   x-ray   diffractogram   for   the VO_2
        nanoparticles is shown in Fig. 21. Three sample of the
35   VO_2 nanoparticles were subjected to heat treatment. All

three samples were treated for 17 hours in the 1 inch
quartz tube with an flow of inert gas (Ar) of 103 sccm.
Samples 1, 2 and 3, in addition, had O_2 flow rates of
4.8 sccm, 10.1 sccm and 20.9 sccm, respectively.

5   Samples 1 and 2 were heated at 224°C while sample 3 was
heated at a temperature of 221°C. The x-ray
diffractograms of the three samples are shown in Figs.
22-24, respectively.

Example 8 - 2-D V_2O_5 from VO_2 Nanoparticles

10   The initial VO_2 nanoparticles were from the
same batch of nanoparticles produced by laser pyrolysis
described in Example 7 with parameters given in the
second column of values in Table 3. The VO_2
nanoparticles were heated at 105°C for about 21 hours.

15   During heating, O_2 was flowed through the tube at a rate
of 106 sccm. The resulting particles had a significant
portion of 2-D crystalline V_2O_5 with a significant
fraction of the particles remaining as crystalline VO_2.
The x-ray diffractogram is shown in Fig. 25.

20   Example 9 - 2-D V_2O_5 from Amorphous V_2O_5 Nanoparticles

             The initial amorphous V_2O_5 nanoparticles were
from the same batch of nanoparticles produced by laser
pyrolysis described in Example 6 with parameters given
in the second column of values in Table 2. The

25   amorphous V_2O_5 nanoparticles were heated at 105°C for
about 21 hours. During heating, O_2 was flowed through
the tube at a rate of 106 sccm. The resulting particles
had an x-ray diffractogram characteristic of 2-D
crystalline V_2O_5, as shown in Fig. 26.

30   Comparative Example 1- Commercial V_6O_{13}

             Commercial V_6O_{13} was purchased from Alfa Aesar,
a Johnson Matthey Company, Ward Hill, MA. A 7.8 mg
quantity of the commercial V_6O_{13} powder was processed
into a cathode and tested in a lithium battery, as

described above. Over the course of the 170 hour test,
the battery was discharged three times. The initial
voltage was 3.54 V. The cell had a discharge capacity
of 246.2 Ah/kg and an energy density of the cathode
5   active material of 610.1 Wh/kg. This energy density
compared with a theoretical maximum value of 890 Wh/kg
based on the reversible intercalation of up to 8 lithium
ions per unit cell of vanadium oxide.

Example 10 - VO_2 Nanoparticles

10   Nanoscale VO_2 particles were produced by laser
pyrolysis according to the parameters in column 1 of
Table 3. As noted above, an analysis of the TEM photo
for the VO_2 nanoparticles reveals an average particle
size of about 22 nm. A plot of voltage as a function of
15   time during the discharge/charge cycling is shown in
Fig. 27. A battery produced with these materials
yielded a Discharge Capacity of 249 Ah/kg and an energy
density of 549 Wh/kg. The Discharge Capacity and Energy
Density are nearly twice the values obtained from larger
20   VO_2 particles. These values are higher than the
theoretical maximum-stoichiometric energy density of 390
Wh/kg for VO_2 for the bulk material at 25°C. See, K.
West et al., "Vanadium Oxides as Electrode Materials for
Rechargeable Lithium Cells," J. of Power Sources 20:165-
25   172 (1987), incorporated herein by reference.

Example 11 - Singe Phase 2D-V_2O_5 Nanoparticles

           Single phase 2-D V_2O_5 nanoparticles were
produced by laser pyrolysis according to the parameters
in column 4 of Table 2. As noted above, an analysis of
30   a TEM photo of the 2-D V_2O_5 nanoparticles reveals an
average particle size of about 20 nm. A battery
produced with these materials yielded a Discharge
Capacity of 146 Ah/kg and an Energy Density of 380
Wh/kg.

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Example 12 - Amorphous V₂O₅ Nanoparticles

Single phase amorphous V_2O_5 nanoparticles were produced by laser pyrolysis according to the parameters in the first column of Table 2. As noted above, an analysis of a TEM photo of the amorphous V_2O_5 nanoparticles reveals an average particle size of about 200 nm for the amorphous V_2O_5 nanoparticles used to form the cathode. Two batteries produced with these materials yielded Discharge Capacities of 186.1 Ah/kg and 177.3 Ah/kg, and Energy Densities of 476 Wh/kg and 446.2 Wh/kg.

Example 13 - Mixed Phase V₆O₁₃ / VO₂ Nanoparticles

Mixed phase crystalline V_6O_{13} / VO_2 nanoparticles were produced by laser pyrolysis according to the parameters in the first column of Table 4. As noted above, an analysis of a TEM photo of the mixed pahse nanoparticles reveals an average particle size of about 20 to about 30 nm for the mixed phase V_6O_{13} / VO_2 nanoparticles. A battery produced with these materials yielded a Discharge Capacity of 174 Ah/kg and an Energy Density of 403 Wh/kg.

Example 14 - Crystalline V₂O₅ Nanoparticles

The crystalline V_2O_5 nanoparticles were produced by further processing nanoparticles produced by laser pyrolysis in an oven with an oxygen atmosphere, as described above. Three types of nanoparticles produced by laser pyrolysis were used for further processing. The nanoparticles of Sample A are the particles described above in Example 6 that were produced from amorphous V_2O_5 particles. The nanoparticles of samples B were the particles described above as the first sample of Example 7 that were produced from crystalline VO_2 nanoparticles.

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The crystalline V_2O_5 nanoparticles were formed into batteries. The crystalline V_2O_5 nanoparticles from Sample A yielded a Discharge Capacity of 399 Ah/kg and a Energy Density of 1005 Wh/kg while the crystalline
5   V_2O_5 nanoparticles from Sample B yielded a Discharge Capacity of 370 Ah/kg and an Energy Density of 919 Wh/kg. Note that crystalline V_2O_3 nanoparticles have resulted in an Energy Density greater than 1000 Wh/kg, which is greater than a factor of two larger than
10   estimated theoretical maximum values for bulk V_2O_5.

A third sample was produced by laser pyrolysis using conditions presented in Table 6.

Table 6

Pressure (Torr)	230
Argon - Win (sccm)	700
Argon - Sld. (slm)	5.6
Ethylene (sccm)	2680
Carrier Gas (Argon) sccm	980
Oxygen (sccm)	700
Laser Output (watts)	180
Nozzle Size	5/8" x 1/8"

The third sample was also further processed in an oven. The nanoparticles were heated for 16 hours at 227°C with
25   an O_2 flow rate of 105.6 sccm. Processing these heat treated particles into a battery as described above, a Discharge Capacity of 438 Ah/kg and an Energy Density of 1121 Wh/kg were measured.

Example 15 - Summary of Oven Treated Nanoparticles And
30   Nanoparticles Produced Directly by Laser Pyrolysis

This example summarizes a set of measurements taken with different batches of vanadium oxide nanoparticles. The nanoparticles were either made directly with laser pyrolysis (Table 7A) or with

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additional heating in an oven under oxidizing conditions (Table 7B).

Table 7A

<u>Vanadium Oxide Properties</u>

Material	Discharge Capacity (Ah/kg)	Energy Density (Wh/kg)
Amorphous V_2O_5	182	461
VO_2*	137	328
2D - V_2O_5**	146	380
VO_2	235	519
VO_2	249	549
VO_2	168	377
$VO_{1.27}$	118	270
V_2O_3	94	209
Mixed Phase VO_2/V_6O_{11}	228	510
Amorphous V_2O_5	188	445
Mixed Phase - V_6O_{11}/VO_2	174	403

* Two measurements were made with the same nanoparticles. The individual values were 140 Ah/kg and 133 Ah/kg (Discharge Capacity), and 323 Wh/kg and 333 Wh/kg (Energy Density).

** Two measurements were made with the same nanoparticles. The individual values were 146 Ah/kg and 146 Ah/kg (Discharge Capacity), and 378 Wh/kg and 381 Wh/kg (Energy Density).

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Table 7B

Vanadium Oxide Properties - Heat Treated

Material	Discharge Capacity (Ah/kg)	Energy Density (Wh/kg)
Orthorhombic V_2O_5	336	848
Mixed Phase VO_2/V_2O_5	297	721
Orthorhombic V_2O_5	399	1005
Orthorhombic V_2O_5	370	919
2-D V_2O_5	292	738
Mixed Phase 2D V_2O_5/VO_2	304	751
	438	1121

The embodiments described above are intended to be representative and not limiting. Additional embodiments of the invention are within the claims. As will be understood by those skilled in the art, many changes in the methods and apparatus described above may be made by the skilled practitioner without departing from the spirit and scope of the invention, which should be limited only as set forward in the claims which follow.

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WHAT IS CLAIMED IS:

1.   A collection of particles comprising vanadium oxide, the measurements along the principle axes of the particles are each about 1000 nm or less for at least about 95 percent of the particles.

2.   The collection of particles of claim 1 having an average diameter from about 5 nm to about 100 nm.

3.   The collection of particles of claim 1 having an average diameter from about 5 nm to about 50 nm.

4.   The collection of particles of claim 1 wherein the vanadium oxide has a stoichiometry of VO_2.

5.   The collection of particles of claim 1 wherein the vanadium oxide has a stoichiometry of V_2O_5.

6.   The collection of particles of claim 1 wherein the vanadium oxide has a stoichiometry of V_6O_{13}.

7.   The collection of particles of claim 1 wherein the vanadium oxide is crystalline.

8.   The collection of particles of claim 1 wherein 95 percent of the vanadium oxide nanoparticles have a diameter greater than about 50 percent of the average diameter and less than about 150 percent of the average diameter.

9.   A method of producing vanadium oxide nanoparticles comprising the step of pyrolyzing a molecular stream comprising a vanadium precursor, an oxidizing agent and a radiation absorbing gas in a reaction chamber, where the pyrolysis is driven by heat absorbed from a laser beam.

10.   The method of claim 9 wherein the vanadium oxide nanoparticles have an average diameter from about 5 nm to about 150 nm.

11.   An apparatus comprising:

         (a) a reaction chamber isolated from the ambient atmosphere;

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(b) a reactant gas inlet defining a path of a molecular stream, the inlet being connected to a source of vanadium precursor, an oxidizing agent and a laser absorbing gas;

(c) a laser beam path intersecting the path of the molecular stream; and

(d) a product outlet.

12.   The apparatus of claim 11 wherein the vanadium precursor is $VOCl_3$ and the oxidizing agent is O_2.

13.   The apparatus of claim 11 wherein the reactant gas inlet is elongated in one dimension.

14.   A process for converting nanoparticles of vanadium oxide to other forms of vanadium oxide comprising the step of heating the nanoparticles of vanadium oxide in an oxidizing or inert atmosphere at a temperature at least about 300°C below the melting point of both the nanoparticles of vanadium oxide and the other forms of vanadium oxide.

15.   The process of claim 14 wherein the temperature is between about 60°C and about 500°C.

16.   The process of claim 14 wherein the heating is performed in an oxidizing atmosphere, wherein the oxidizing atmosphere comprises between about 1 percent oxidizing gas and about 99 percent oxidizing gas by partial pressure.

17.   The process of claim 14 wherein the other forms of vanadium oxide comprise 2-D crystalline V_2O_5 or crystalline V_2O_5.

18.   The process of claim 14 wherein the nanoparticles of vanadium oxide have an average diameter from about 5 nm to about 150 nm.

19.   Vanadium oxide nanoparticles formed by heating in an oxidizing or inert atmosphere, vanadium oxide nanoparticles of a different form.

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20.   The vanadium oxide nanoparticles of claim 19 wherein the vanadium oxide nanoparticles of a different form have an average diameter from about 5 nm to about 150 nm.

21.   The vanadium oxide nanoparticles of claim 19 wherein the vanadium oxide nanoparticles formed by heating have a higher oxygen to vanadium ratio than the vanadium oxide nanoparticles of a different form.

22.   The vanadium oxide nanoparticles of claim 19 wherein the vanadium oxide nanoparticles formed by heating comprise V_2O_5.

23.   A process for forming vanadium oxide particles comprising the step of heating particles of vanadium oxide with a lower oxygen to vanadium ratio than the vanadium oxide particles to be formed in an oxidizing atmosphere at a temperature at least about 300°C below the melting point of both the vanadium oxide particles to be heated and the product vanadium oxide particles to be formed.

24.   The process of claim 23 wherein the temperature is between about 60°C and about 800°C.

25.   The process of claim 23 wherein the initial vanadium oxide particles have an average diameter from about 5 nm to about 1000 nm.

26.   A process for forming crystalline V_2O_5 comprising the step of heating amorphous V_2O_5 at a temperature at least about 300°C below the melting point of both the amorphous V_2O_5 and the crystalline V_2O_5.

27.   The process of claim 26 wherein the temperature is between about 60°C and about 800°C.

28.   The process of claim 26 wherein the amorphous V_2O_5 particles have an average diameter from about 5 nm to about 1000 nm.

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29.   A cathode composition comprising vanadium oxide particles having an average diameter less than about 1000 nm and a binder.

30.   The cathode composition of claim 29 wherein the vanadium oxide particles have an average diameter from about 50 nm to about 5 nm.

31.   The cathode composition of claim 29 wherein the binder comprises polyvinylidene fluoride, polyethylene oxide, polyethylene, polypropylene, polytetrafluoroethylene, polyacrylates or mixtures or copolymers thereof.

32.   The cathode composition of claim 29 further comprising supplementary electrically conductive particles.

33.   The cathode composition of claim 29 wherein the cathode comprises from about 60 percent by weight to about 98 percent by weight vanadium oxide particles.

34.   A battery comprising an anode, a cathode comprising vanadium oxide particles having an average diameter less than about 1000 nm and a binder, and a separator element disposed between the anode and cathode.

35.   The battery of claim 34 wherein the anode comprises lithium metal.

36.   The battery of claim 34 wherein the anode comprises a composition that intercalates lithium.

37.   A battery comprising an anode, an electrolyte, a cathode and a separator element disposed between the anode and the cathode, the electrolyte comprising lithium ions and the cathode comprising nanoparticles of intercalation type electroactive material and a binder, wherein the electroactive material in the cathode exhibits an energy density greater than about 900 Wh/kg during discharge of the battery.

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38.   The battery of claim 37 wherein the battery is a secondary battery.

39.   The battery of claim 37 wherein the electroactive material in the cathode exhibits an energy density from about 950 Wh/kg to about 1200 Wh/kg.

40.   The battery of claim 37 wherein the electroactive nanoparticles comprise vanadium oxide.

41.   The battery of claim 37 wherein the electroactive material in the anode comprises a composition that intercalates lithium.
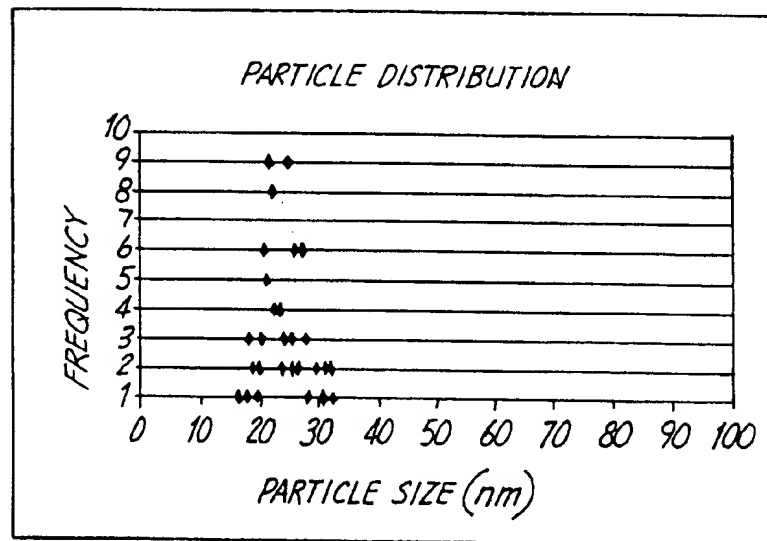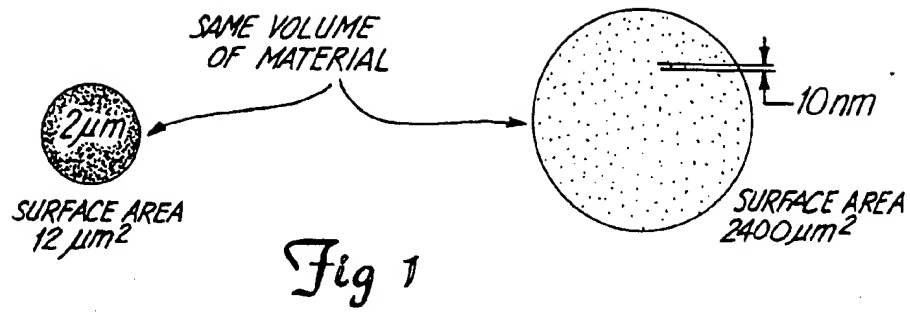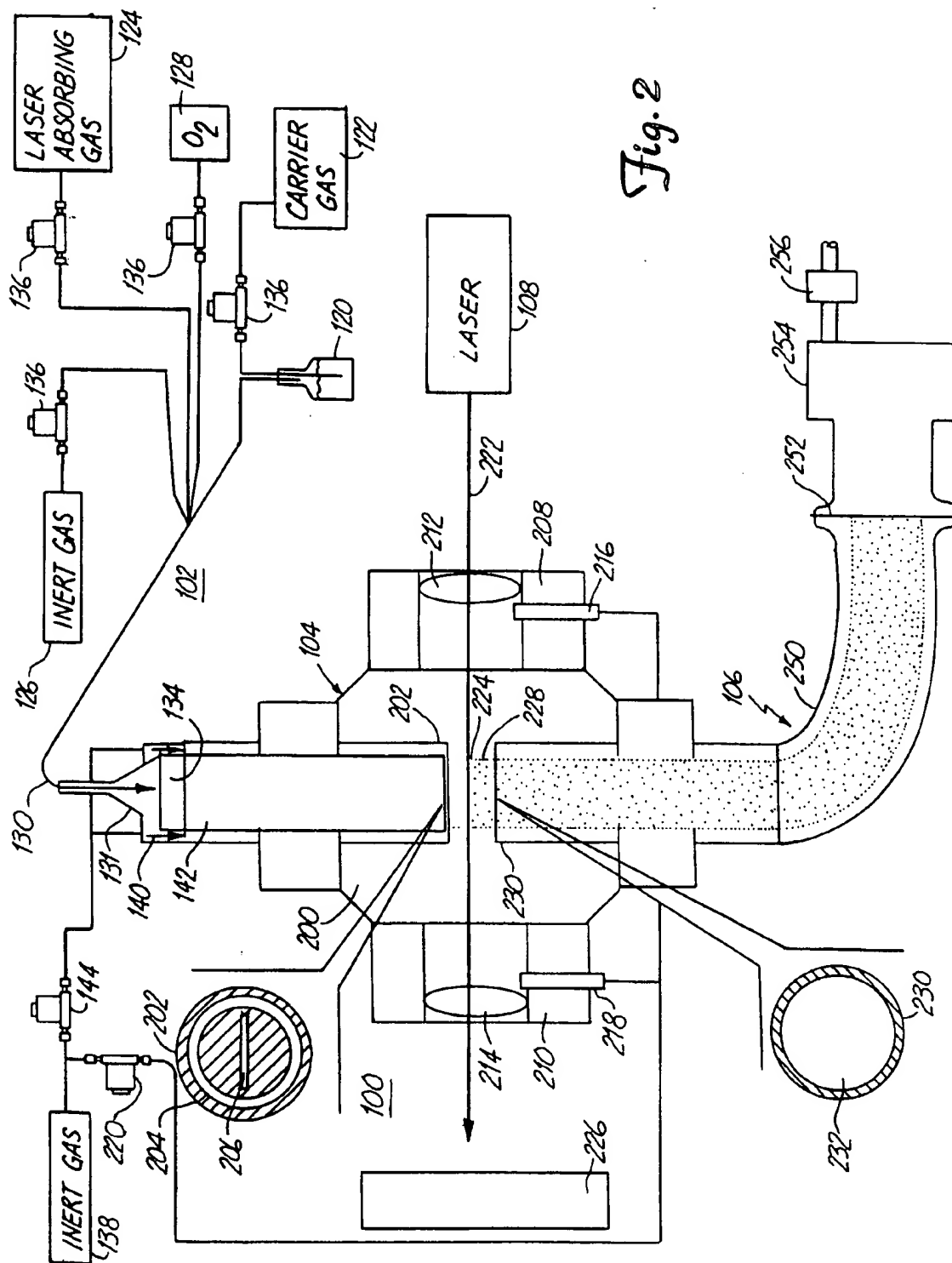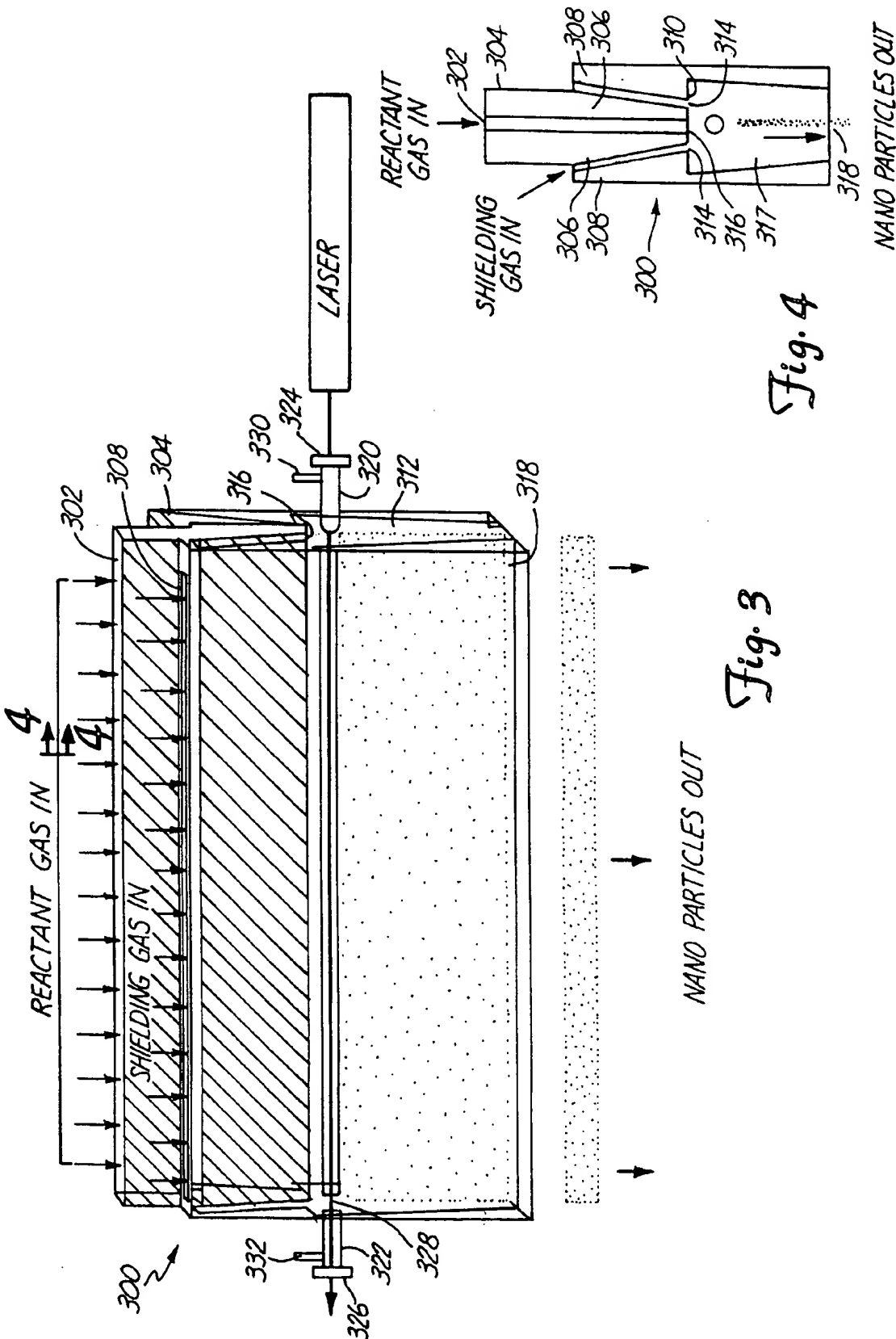
Fig 1

Fig 14

Fig. 2

Fig. 4

Fig. 3

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Vanadium Dioxide

100 nm

Fig. 12

Fig. 13

Vanadium Dioxide

cHø 590KX FF0395

20 nm
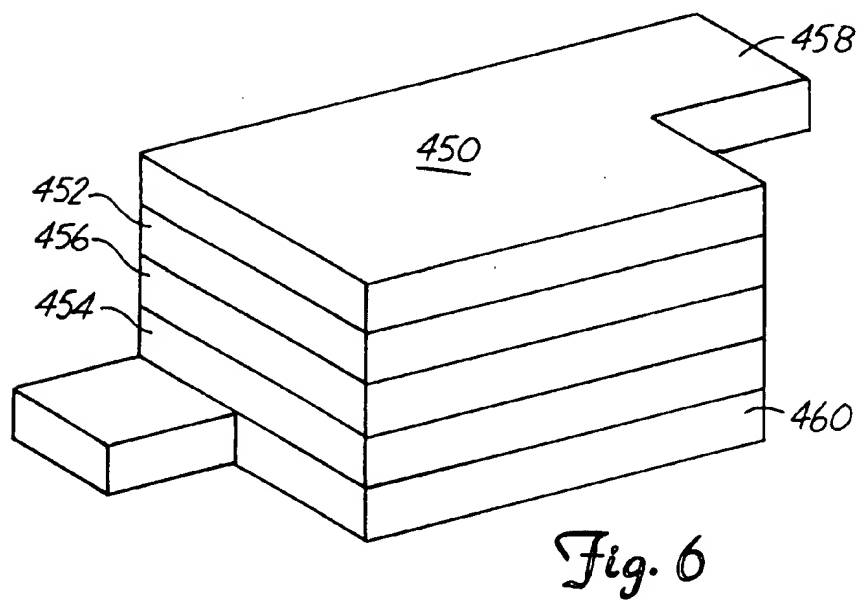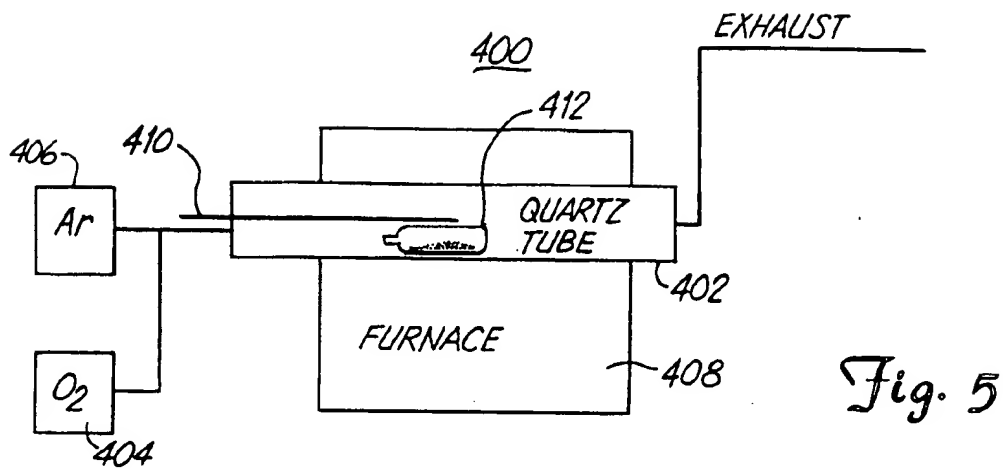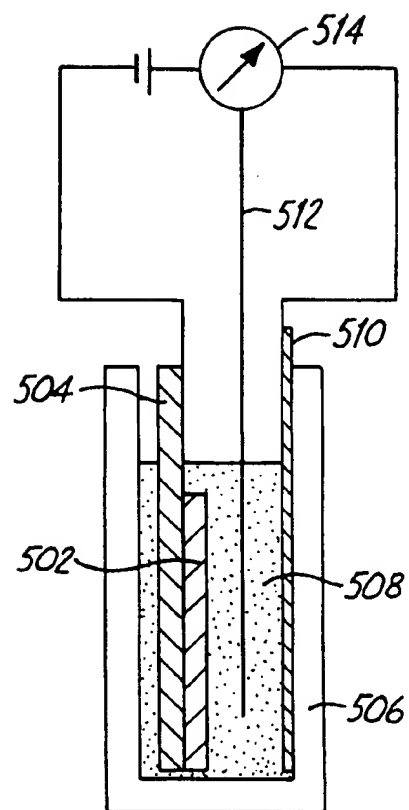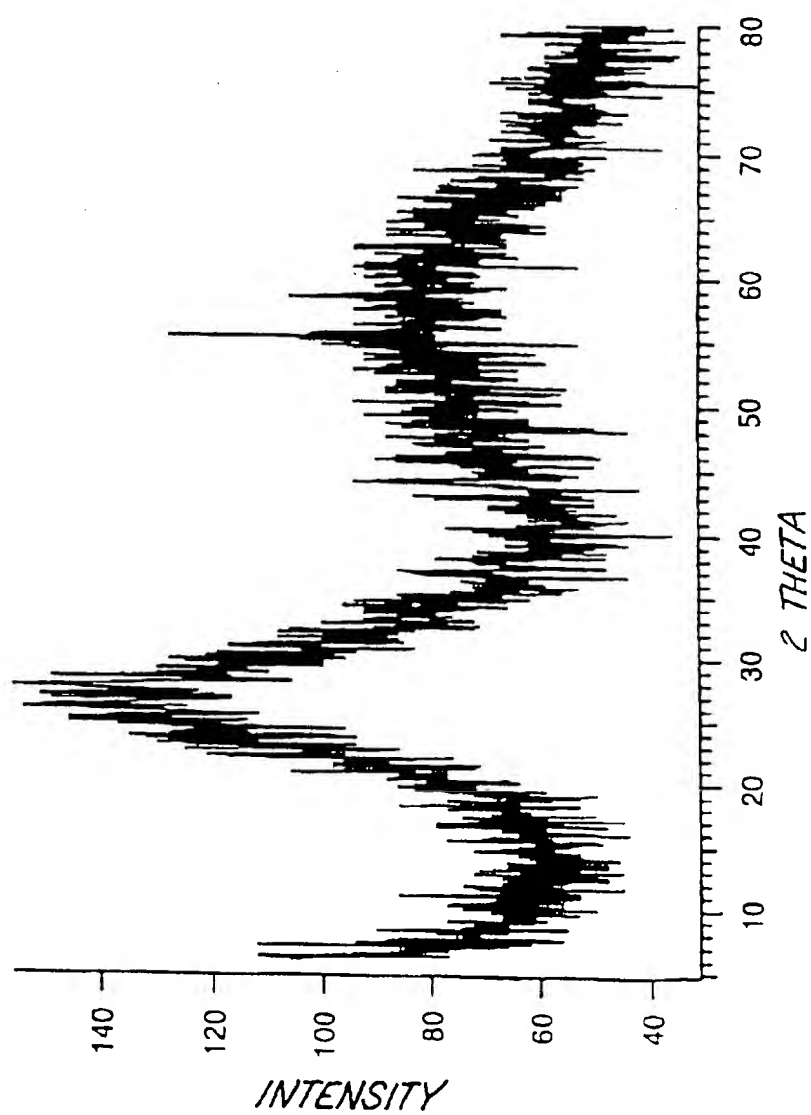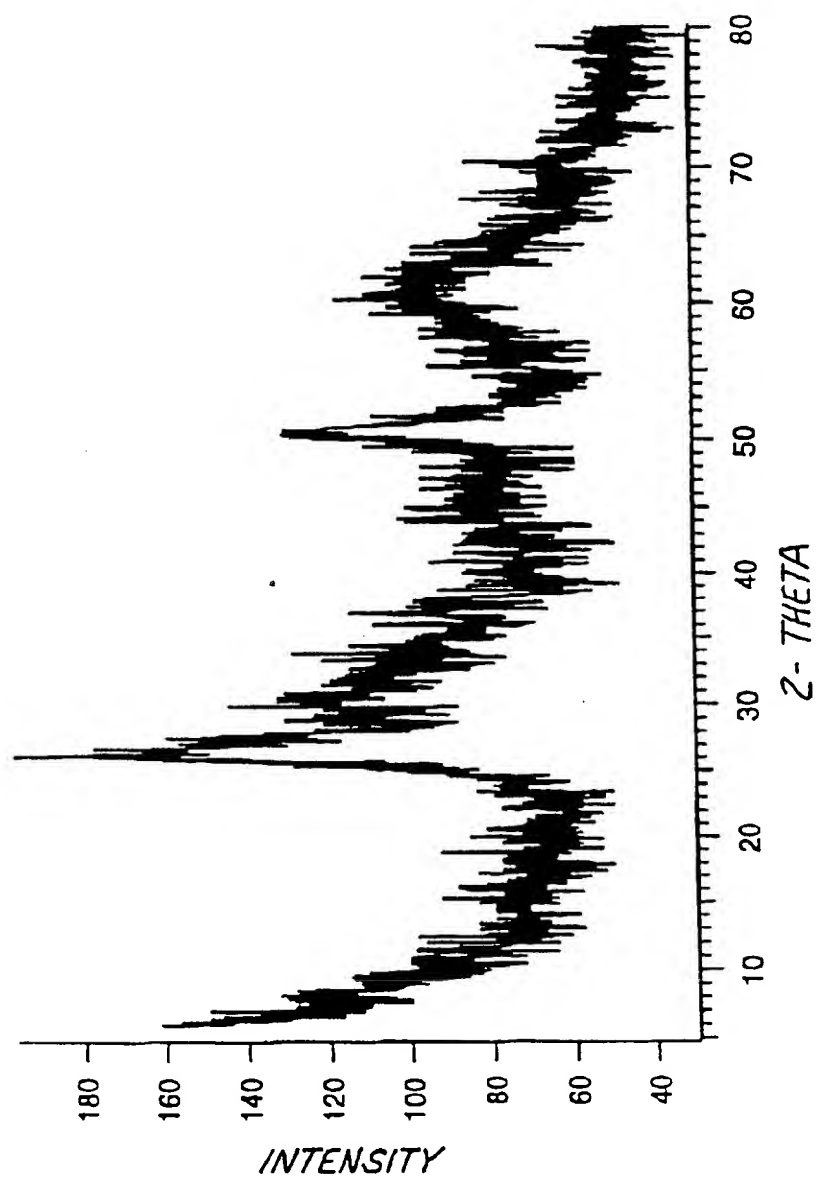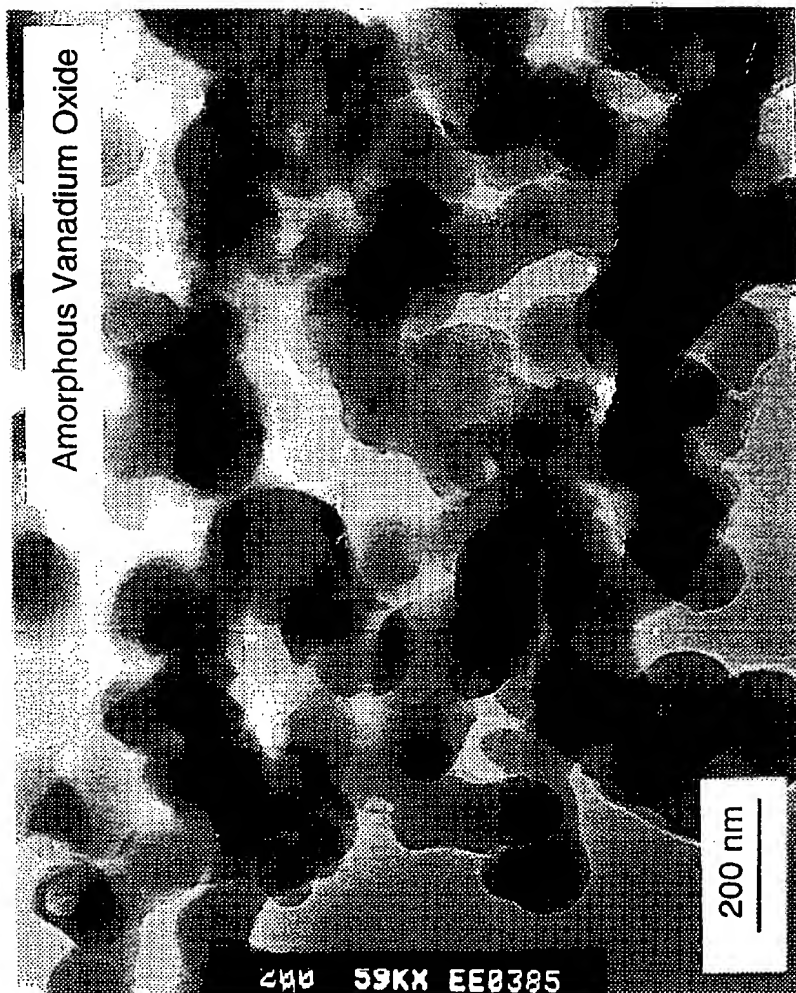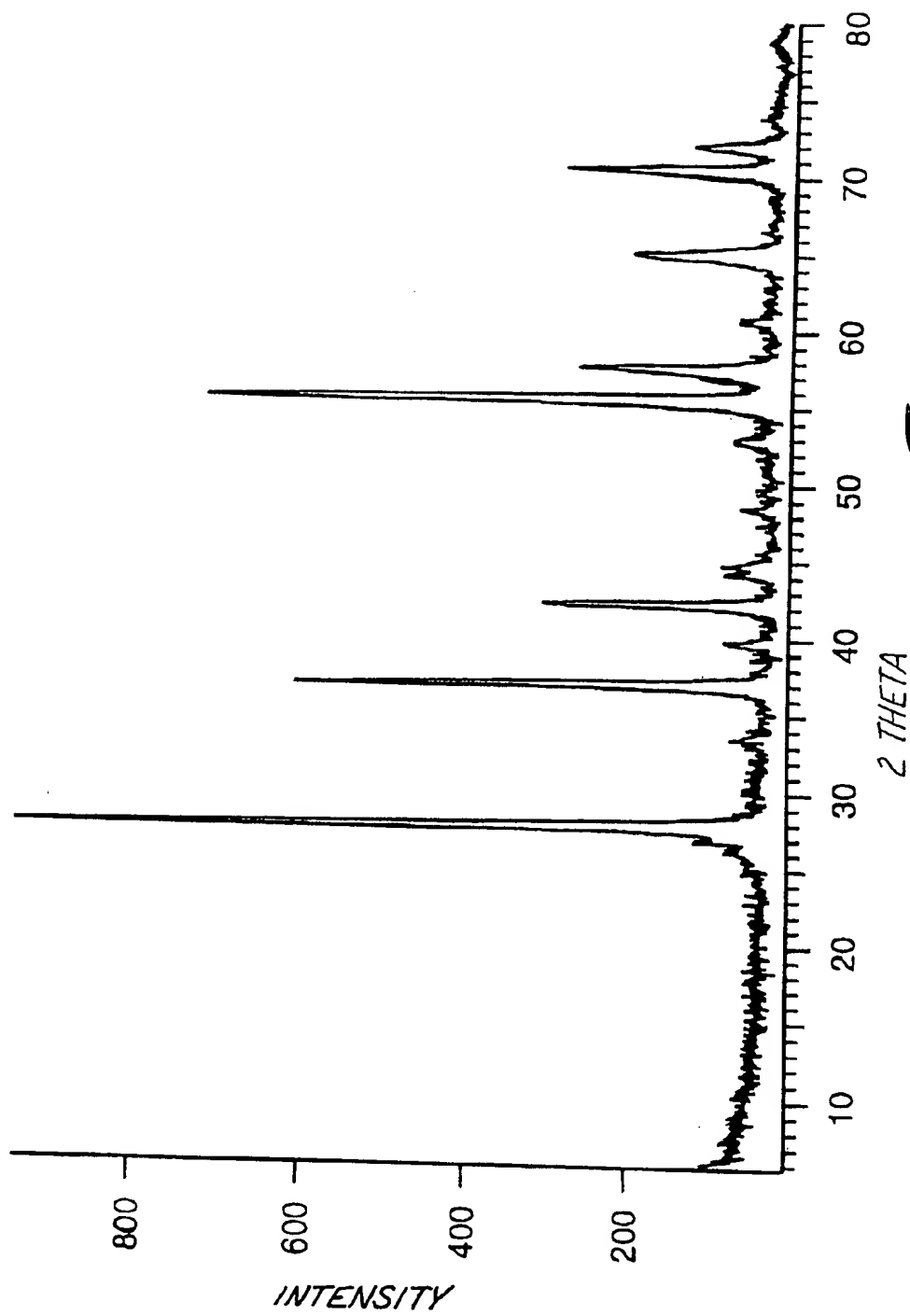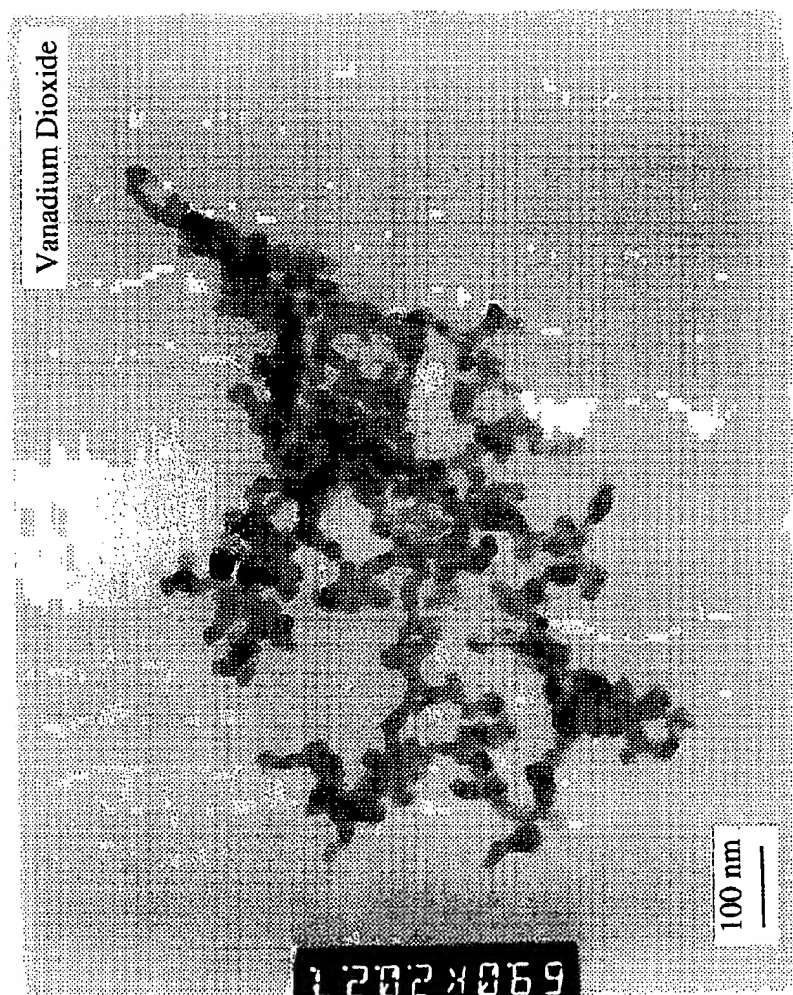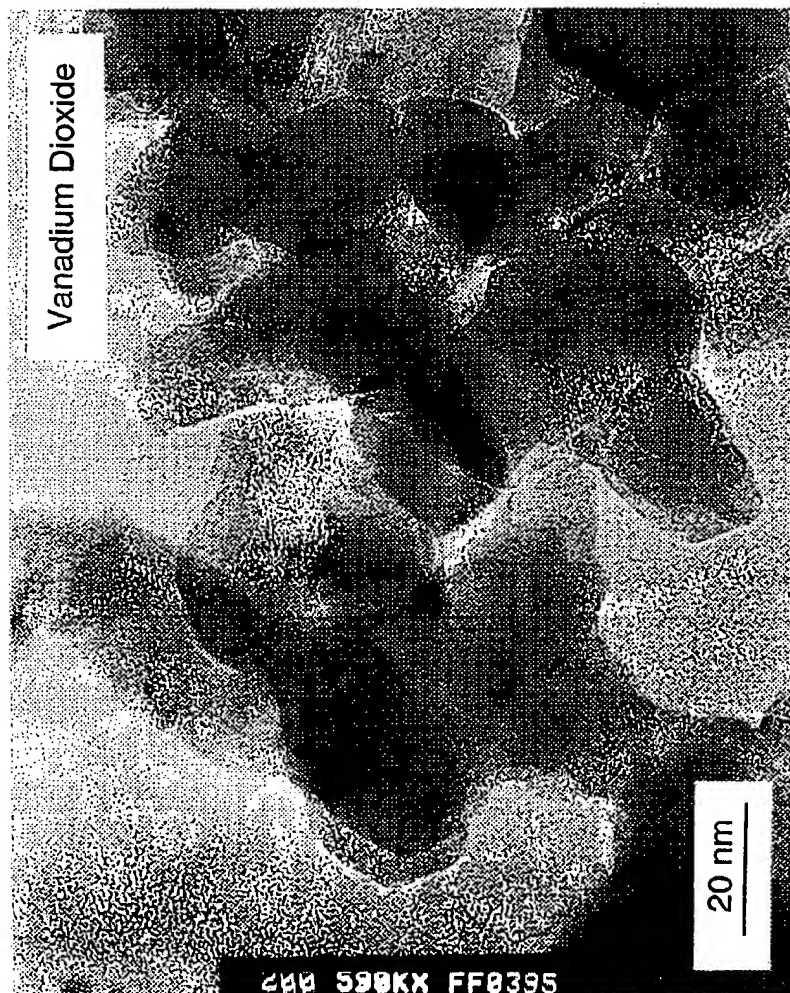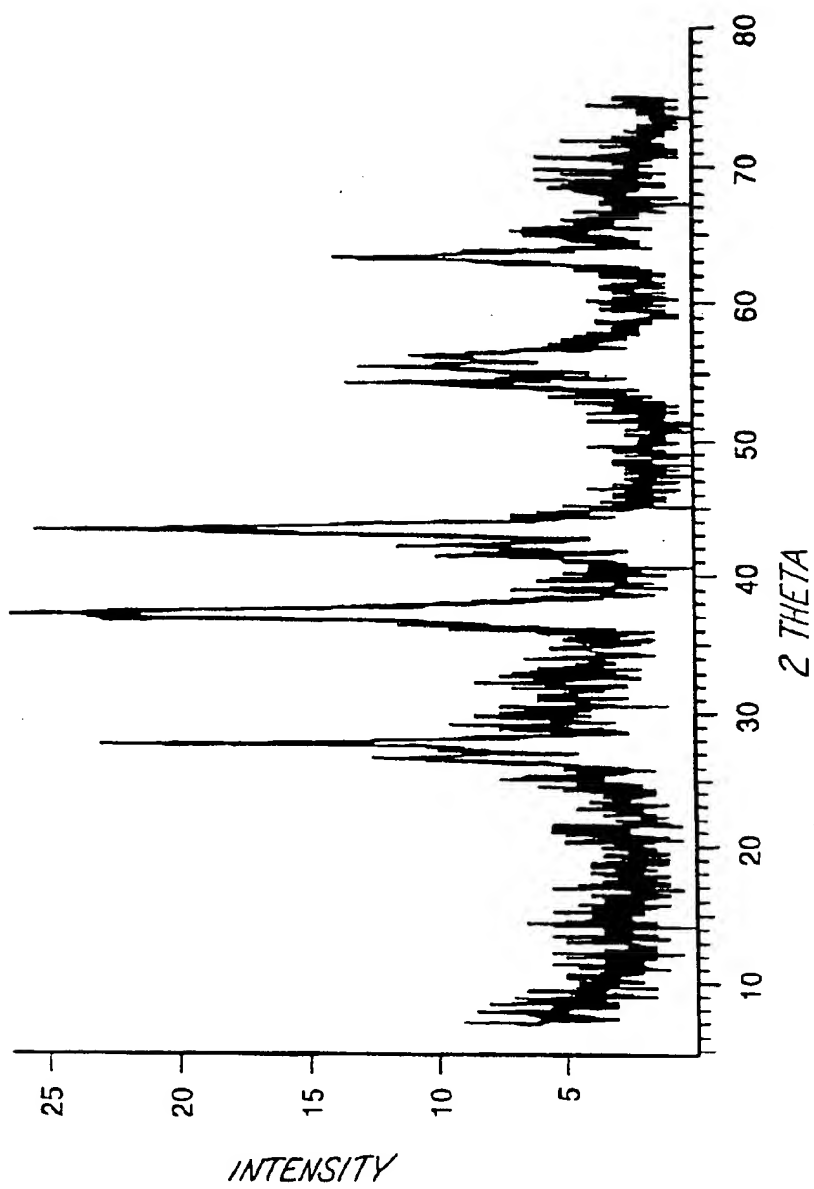
Fig. 15

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Fig. 17

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Fig. 16
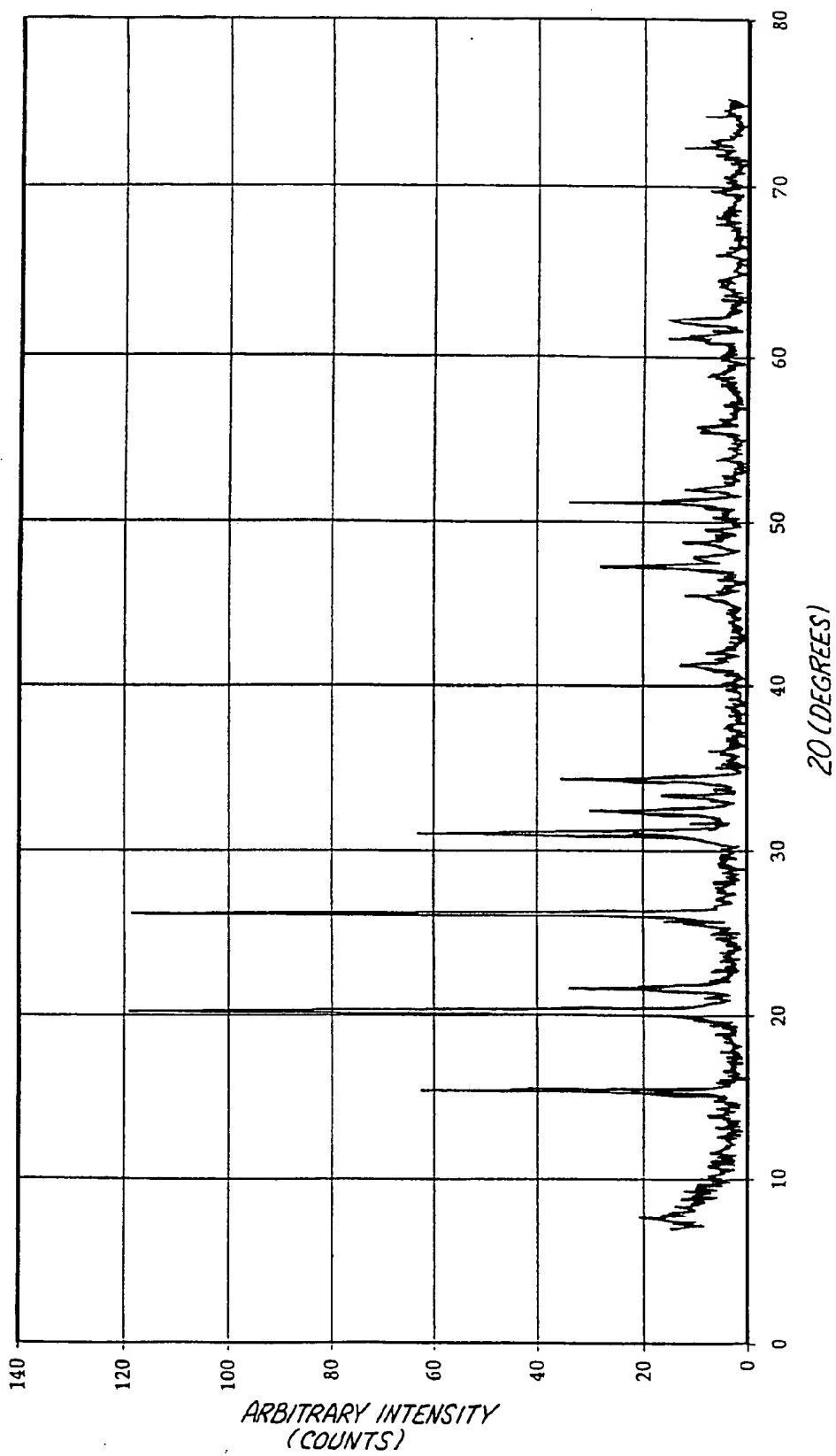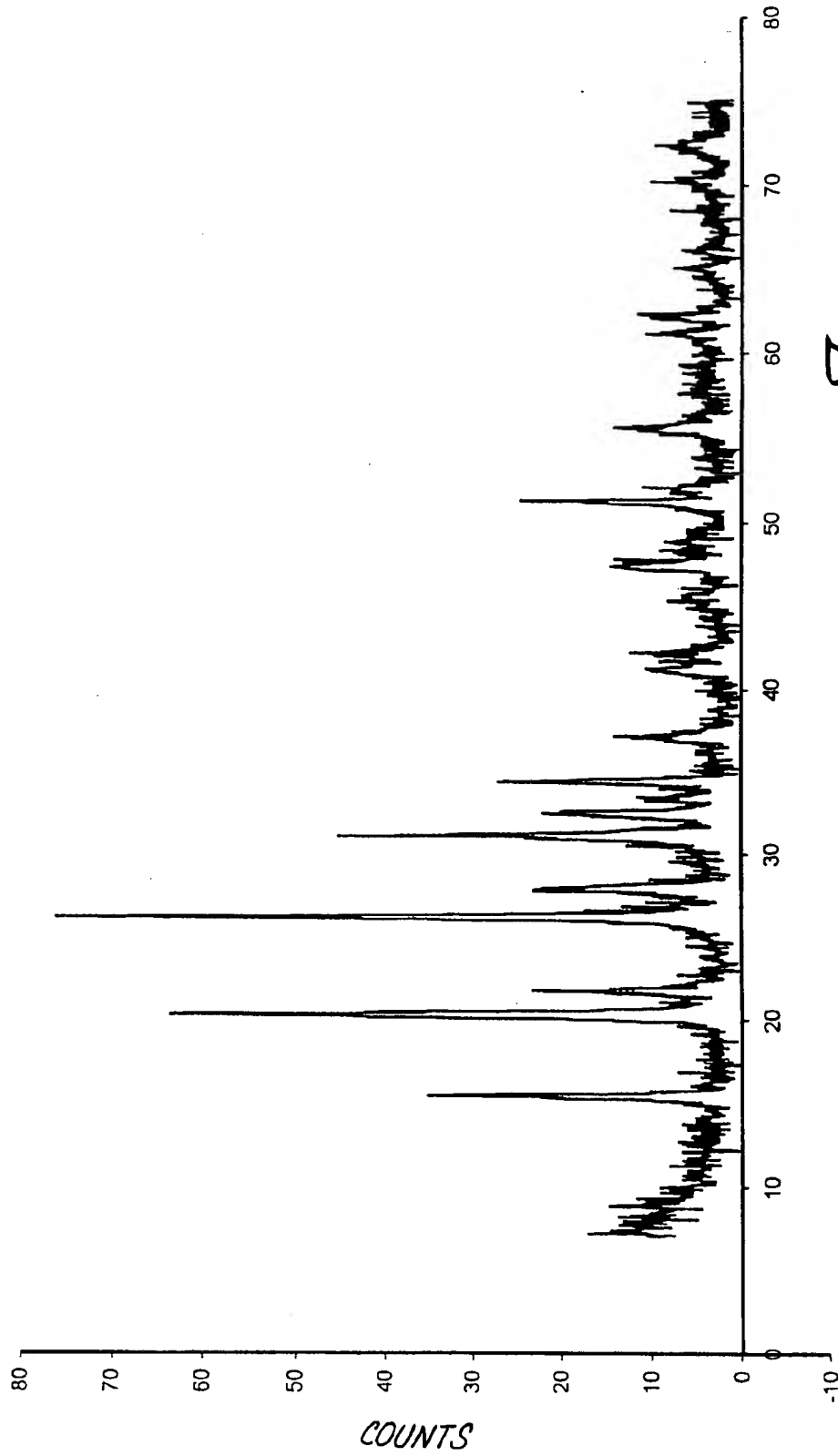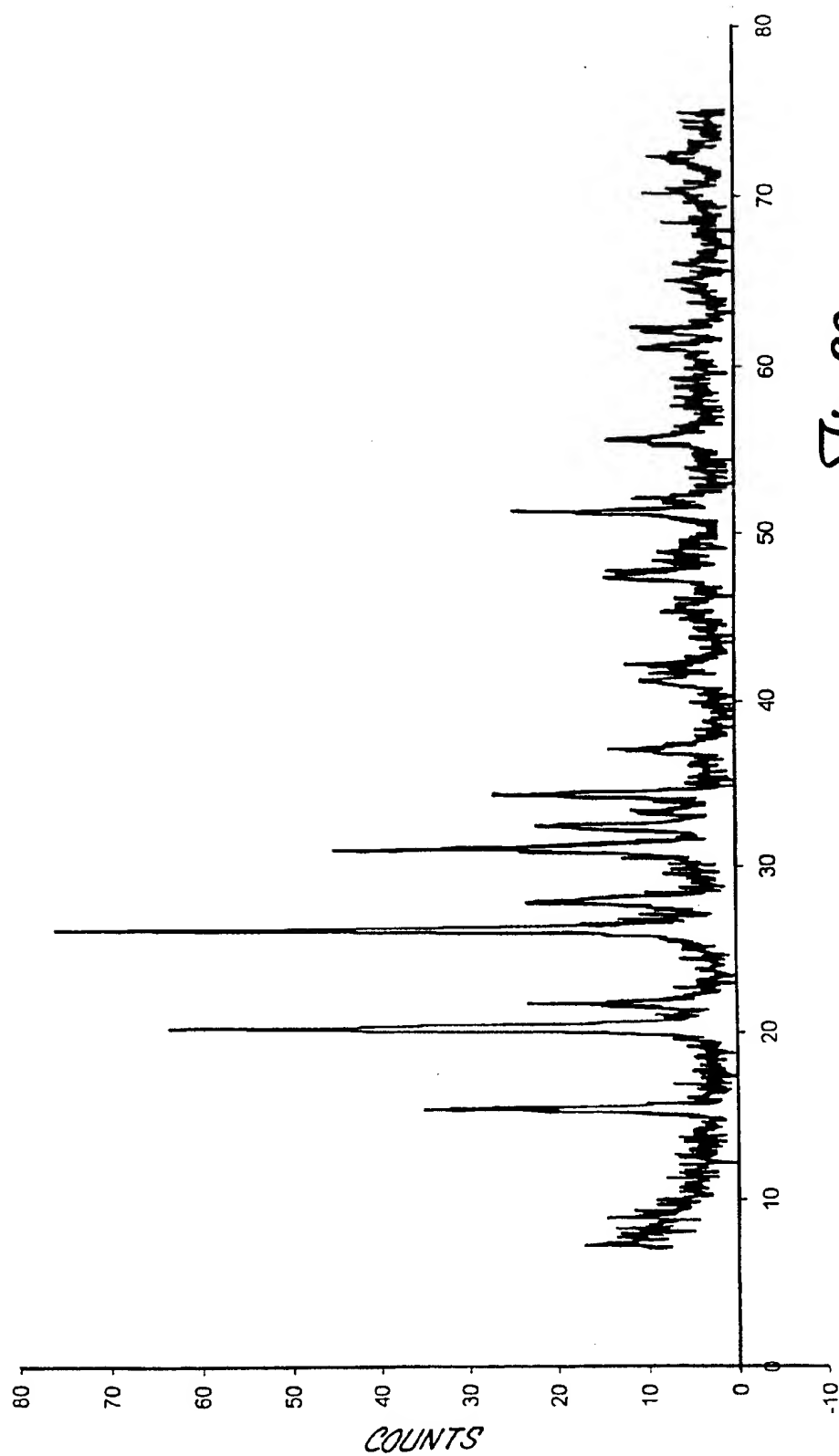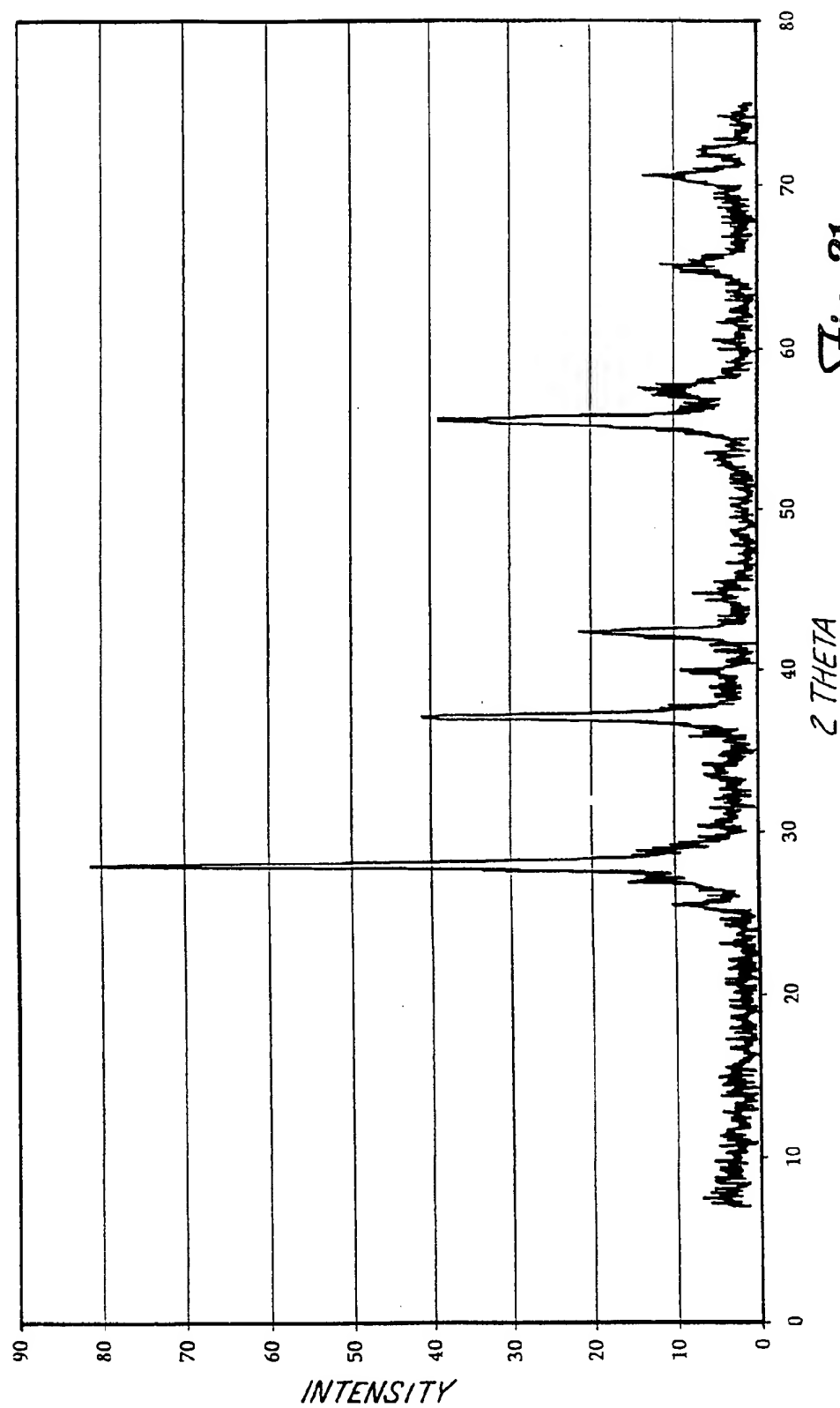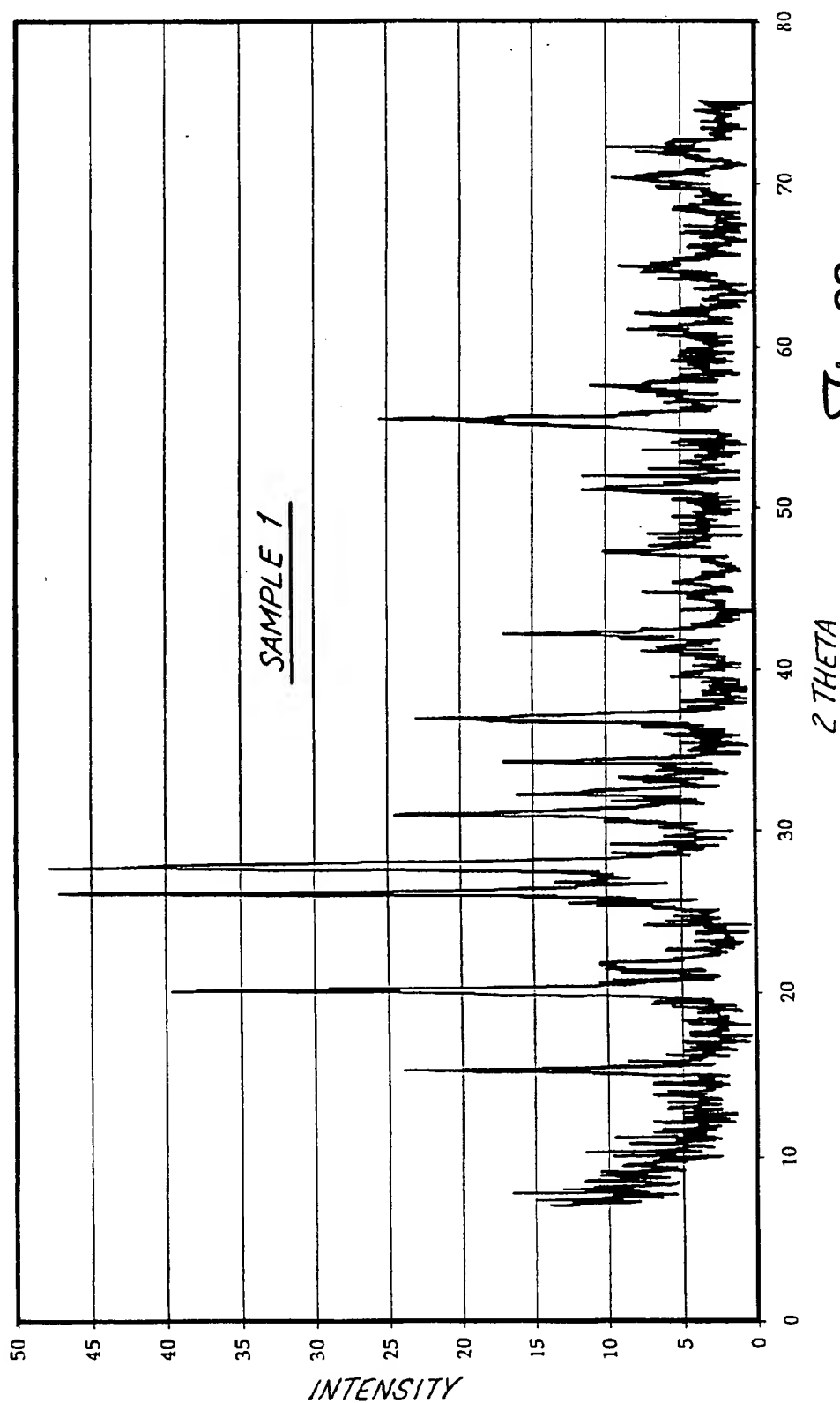
Fig. 18

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Fig. 19

Fig. 20

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Fig. 21

SAMPLE 1

Fig. 22

Fig. 23

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Fig. 24

SAMPLE 3

2 THETA

INTENSITY

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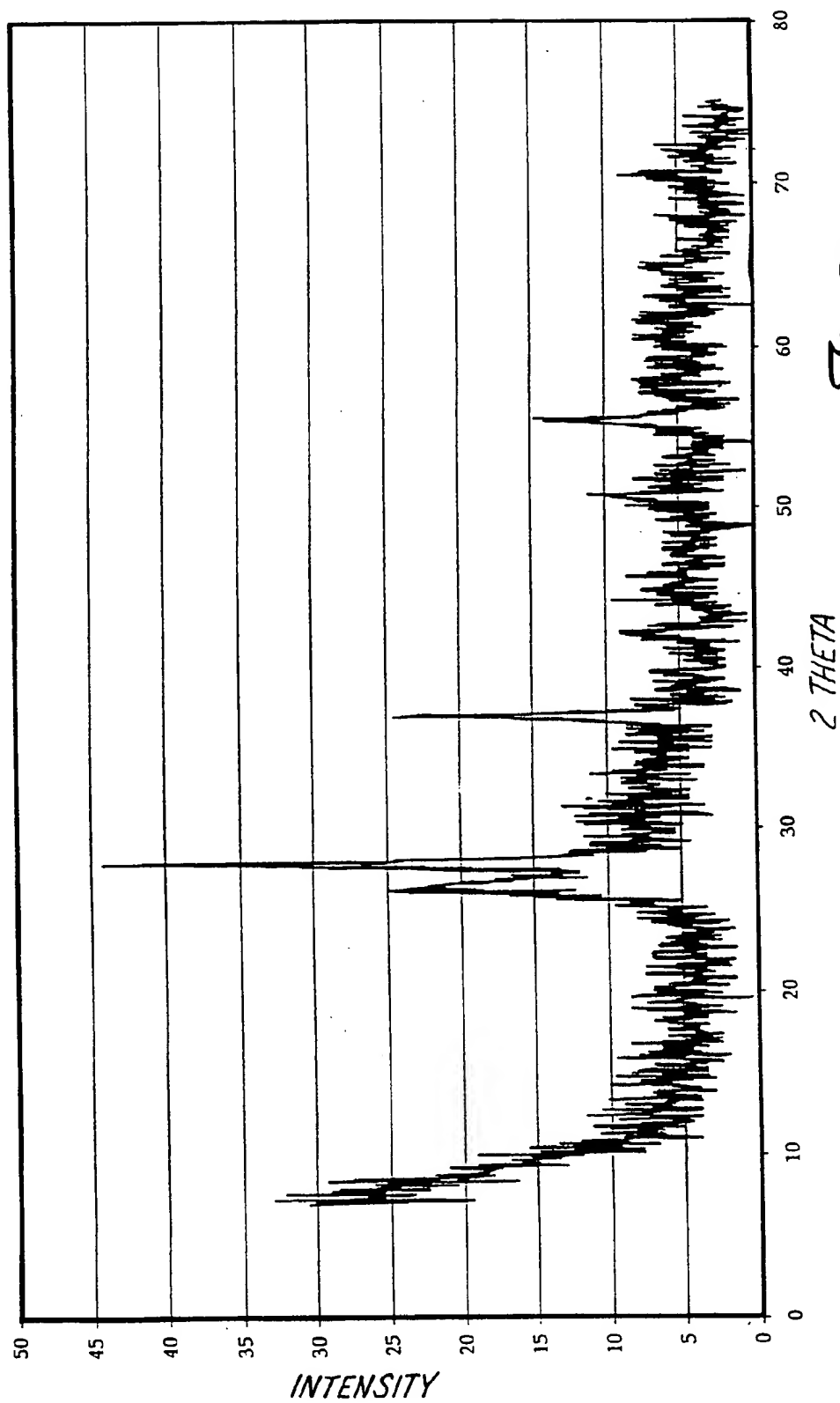

Fig. 25

Fig. 26

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Fig.27
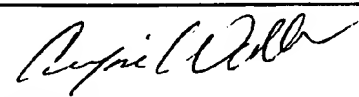
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SAMPLE A
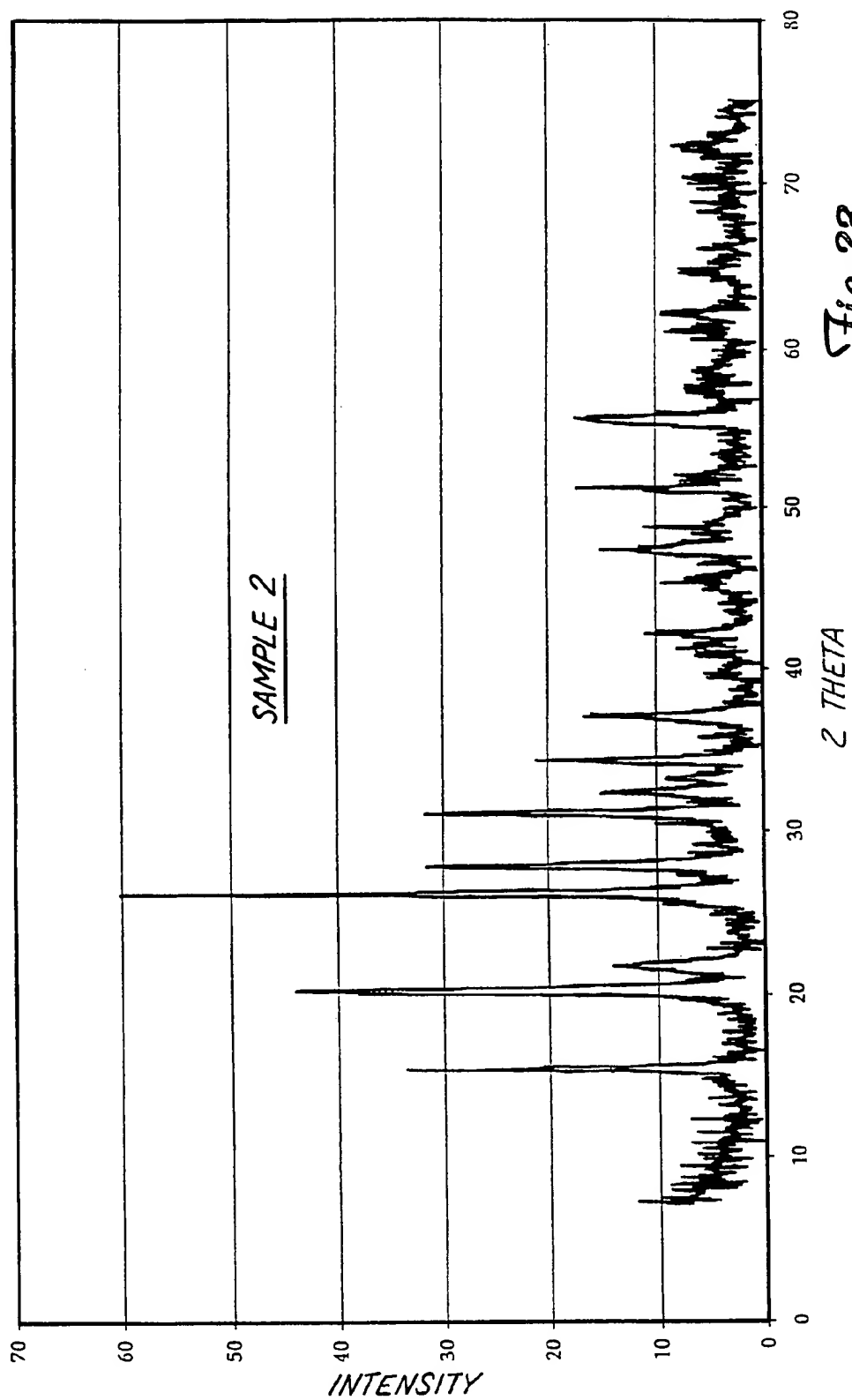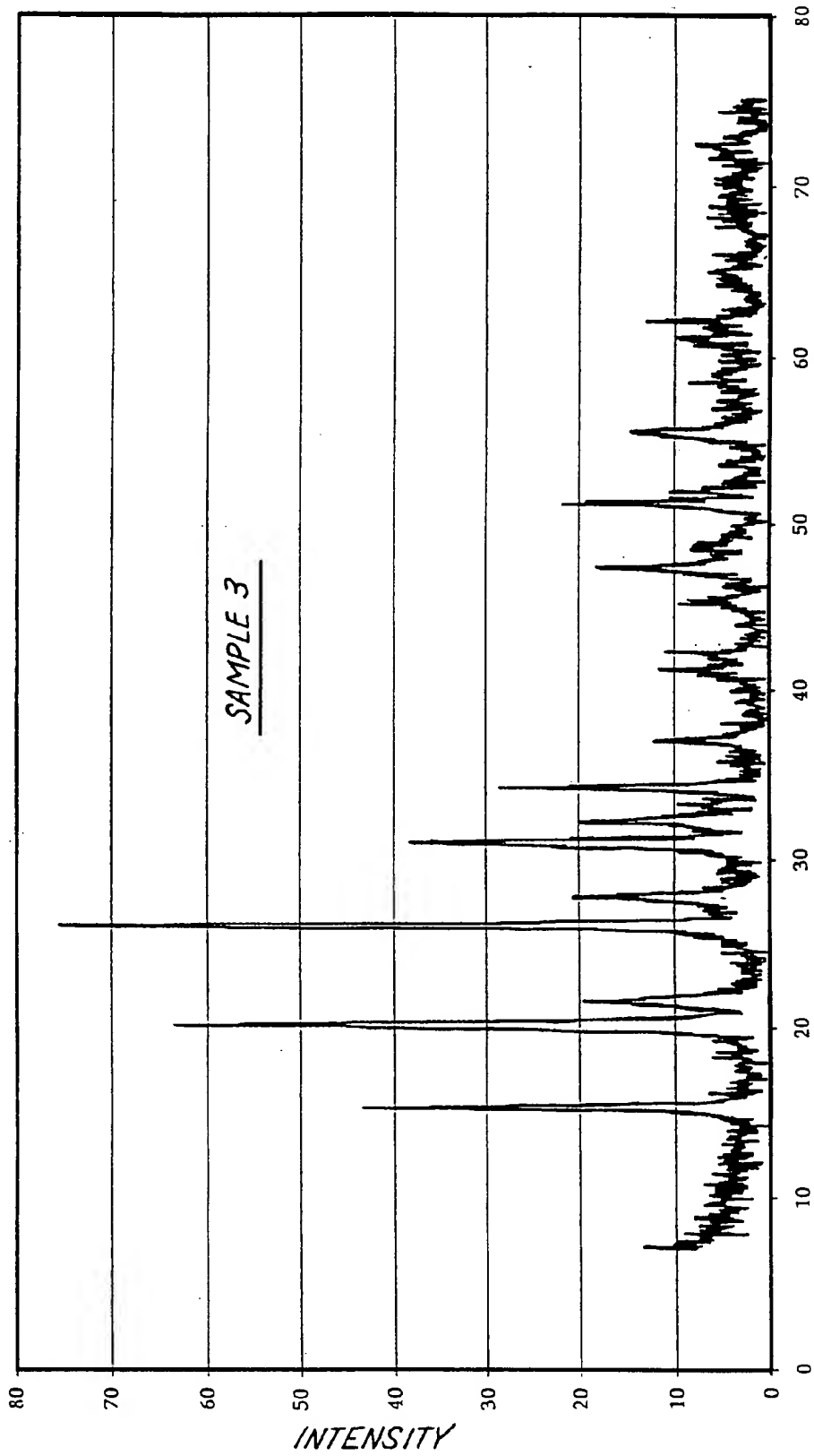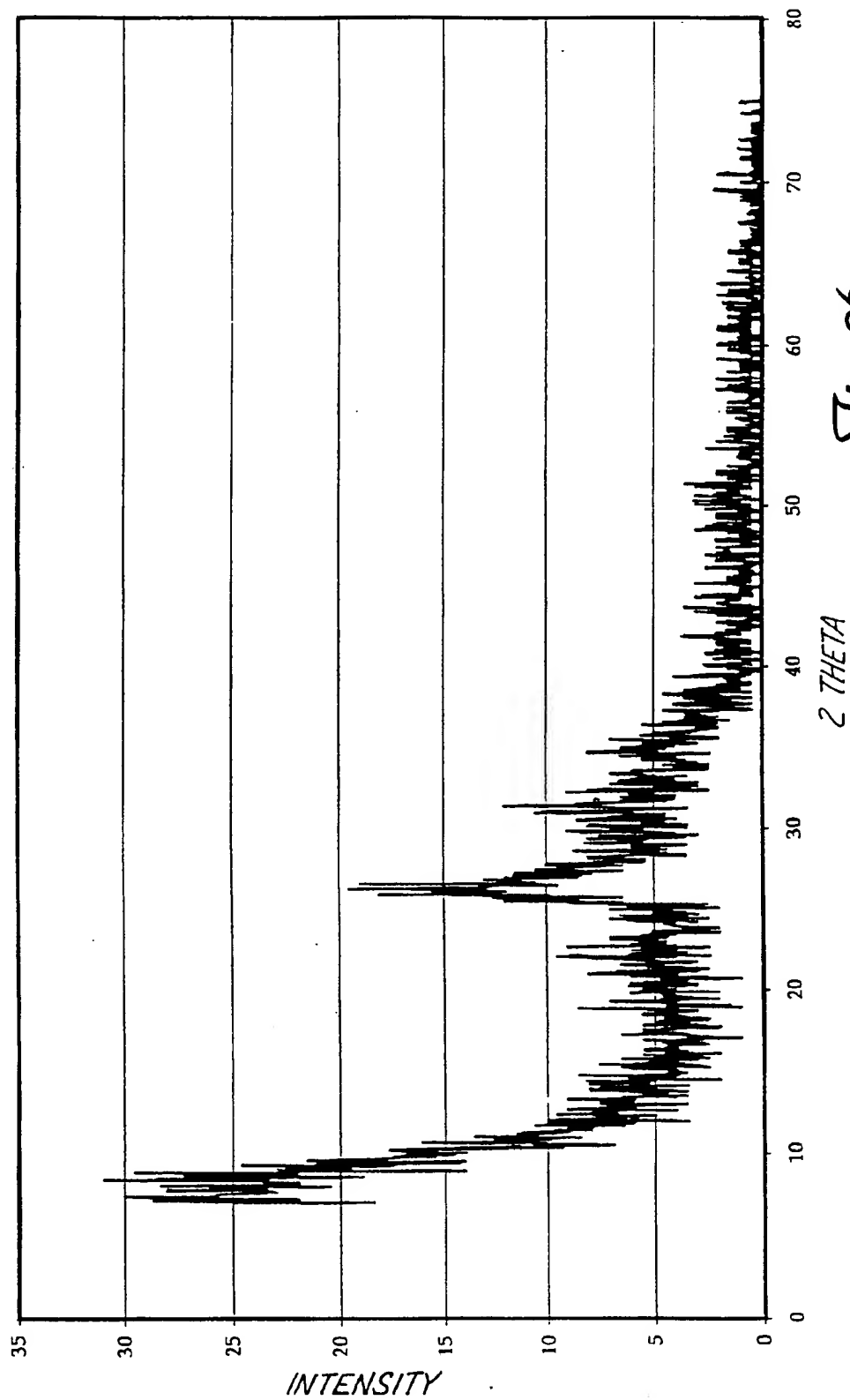
Fig. 28

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01M 4/48
US CL :429/231.2; 423/62,579; 149/37; 419/31; 264/28.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/231.2; 423/62,579; 149/37; 419/31; 264/28.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS. STN (files WPIDS, CA
search terms: vanadium oxides, particle size distribution, nanoparticles, batteries, cathodes

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,483,110 A (ROZGONYI) 09 December 1969, col. 4, lines 29-42.	14-28
X	US 5,589,300 A (FAUTEUX et al.) 31 December 1996, col. 2, lines 54-63; col. 4, lines 53-59; col. 5, lines 58-61; col. 7, lines 57-63.	1-10
X	US 5,549,880 A (KOKSBANG et al.) 27 August 1996, col. 5, lines 4-6; col. 6, lines 4-35.	1-8 and 29-41
Y	US 5,437,943 A (FUJII et al.) 01 August 1995, col. 5, lines 62-68; col. 6, lines 11-16.	1-8 and 29-41
Y	US 5,443,809 A (OLSEN) 22 August 1995, col. 4, line 63-col. 5, line 2 and Figure 2.	1-13 and 29-41

X	Further documents are listed in the continuation of Box C.	☐	See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 OCTOBER 1998	**1 0 NOV 1998**

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	CAROL CHANEY
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,514,496 A (MISHIMA et al.) 07 May 1996, col. 5, lines 17-26.	1-8 and 29-41

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/14947

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

    Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

                             ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)＊

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group A, claims 1-8 and 29-41, are directed to nanoparticle-sized vanadium oxide and electrochemical cells using the battery.

Group B, claims 9 and 10, are directed to a method of producing vanadium oxide by pyrolyzing a molecular stream of vanadium precursor, and oxidizing agent and an energy absorbing gas.

Group C, claims 11-13, directed to an apparatus with a reaction chamber.

Group D, claims 14-18 and 23-28, directed to a method for changing the phases of vanadium oxide which occur in nonparticles.

Group F, claims 19-21 specify vanadium oxide particles which have been obtained by heating.

The inventions listed as Groups A-d do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Claims 1-8 and 29-41 of group A specify particle sizes and the distribution of particle sizes. None of the other groups claim this feature.

Claims 9-10 of group B specify "pyrolizing" as a method step, which the other claims do not.

Claims 11-13 of Group C are the only claims which specify an apparatus.

Claims 14-18 and 23-28 disclose methods of inducing a phase transformation in vanadium oxides. This concept is unique to these claims.

The is no single feature common to all claims.